HEAT STERILIZED NICKEL-CADMIUM CELL FAILURE ANALYSIS PROGRAM

Phase II
Final Report

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Prepared By

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PREFACE

This report was generated in accordance with the requirements of JPL Contract 951092 to summarize the work performed during Phase II of heat sterilizable nickel-cadmium cell failure analysis program. The program effort examined the failure mode analysis for control and heat sterilized cells subjected to 100 percent depth of discharge cycling.

The report was prepared by R. F. Fogle, who served as project engineer for TRW. W. R. Scott was Project Director. Mr. Winfield Yeaney was the Technical Representative for JPL.

ABSTRACT

The heat sterilized nickel-cadmium cell failure analysis program definitely showed a degradation of the cell separator resulting from heat-sterilization. This degradation was evidenced primarily by a lower tensile strength of the separators in those cells which had been sterilized. For cells sterilized in the charged or partially charged condition, the degree of separator degradation increased as the state of charge prior to heat-sterilization increased. Evidence of nickel electrode degradation resulting from sterilization was also established. The plate capacities of those cells which had been sterilized were slightly lower than those of non-sterilized cells. Individual electrode potential measurements on nickel and cadmium plates showed that the nickel electrode contributed to the limit on charge and was the major limiting electrode on discharge, indicating a slight degradation of the nickel electrode resulting from sterilization.

One cell, which had been sterilized, would not accept a charge during plate testing. The plate potentials of this cell with respect to a reference showed the nickel electrode to be abnormal (compared to other cells tested) in the failed cell. Spectrographic and X-ray analysis of the residues from the leach and plate testing solutions of the failed cell showed the major component to be cadmium hydroxide with intermediate concentrations of calcium carbonate and nickel metal.

Chemical analyses of the electrolyte for carbonate and hydroxide content, separator resistivities and cell AC impedances of all cells tested showed considerable variation, making it difficult to establish trends or correlations between these characteristics and the effects of heat-sterilization.

1.0 SUMMARY

The results of the failure analysis test program are summarized below.

1) Heat sterilization of cells in the partially or fully charged state resulted in degradation of the separator. The severity of the degradation increased as the state of charge during heating increased.

2) Heat sterilization of cells in the discharged state resulted in some degree of separator degradation as evidenced by the lower tensile strength and stiffness of the separator in these cells.

3) The concentration of carbonate ion in the electrolyte solution was 20% higher in sterilized than in non-sterilized cells. However, the control cell showed a carbonate concentration 23% higher than sterilized cells. The variations noted in the carbonate content of the cells may be a result of the different methods used for leaching the electrolyte from the separator-electrode assembly. Because of the variations noted in the carbonate content between cells, it is difficult to determine to what degree carbonate contributed to adverse cell performance or whether sterilization promoted carbonate formation.

   In general, the carbonate content was equal to or greater than the hydroxide content in cells tested, The most significant exception to this generalization was observed in the cell having serial number 2732. In this cell, the amount of carbonate was considerably lower than the amount of hydroxide. This cell was special in that its manufacture and sterilization were different from the other cells tested. It was not formed at the time of manufacture, the plates were not matched, and a vacuum fill technique was used for the addition of the electrolyte. Approximately one month after manufacture, the cell was sterilized, formed, and then cycled fifteen (15) times by JPL prior to analysis. Also, cell 2732 was not from the same lot as the other cells tested.

4) The separator resistivity [(1)] data showed considerable variation between cells and between test samples of any one separator. The average resistivity for all the sterilized cells was 605 ohm-cm^2, whereas the average resistivity for the non-sterilized cells was 314 ohm-cm^2. However, if cell S/N 2970 non-sterilized, float charged 19 days, cycle life) and cell S/N 2917 (sterilized, float charged 19 days, cycle life) which both show unusually high resistivity values are neglected; the average resistivity of the sterilized cells is 217 ohm-cm^2 and that of the non-sterilized cells 269 ohm-cm^2. The average variation of resistivity within a separator was 766 ohm-cm^2 for all the sterilized cells and 248 ohm-cm^2 for the non-sterilized cells. Again, if cells S/N 2970 and

(1) The term "separator resistivity" as used in this report refers to the reciprocal of the conductivity of the separator when immersed in electrolyte solution.

1.0 Continued

and S/N 2971 are neglected, the average variation becomes 114 ohm-cm^2 for sterilized and 166 ohm-cm^2 for non-sterilized cells. There is also considerable variation of the resistivity from one cell to another. The separator resistivity for the sterilized cells varies from 110 ohm-cm^2 to 3325 ohm-cm^2 when all cells are considered and from 110 to 442 ohm-cm^2 when cell S/N 2971 is neglected. For the non-sterilized cells the separator resistivity varies from 137 to 605 ohm-cm^2 when all cells are considered and from 137 to 462 ohm-cm^2 when cell S/N 2970 is neglected. It is apparent there is considerable variation of the resistivity data. Two possible explanations for the variation observed are (a) non-uniformity of separator thickness (non-uniformity of separator thickness was confirmed by measurement), and (b) adherence of active electrode material to the separator. No reason for the unusually high resistivity values found for separators from cells S/N 2970 and 2971 was apparent.

5) In general, the plate capacities (flooded condition) of cells that had been sterilized in the discharged state were lower than those of comparable cells that had not been sterilized. The average capacity of the sterilized cells was 3.39 ampere hours while the average capacity of the non-sterilized cells was 4.60. This effect was opposite to that observed at the the termination of Phase I testing, where the cells which had been sterilized showed a higher output capacity (average 2.58 ampere hours) than comparable cells which had not been sterilized (average 1.60 ampere hours). Prior to cutting the cells open for failure analysis, the sterilized cells showed slightly higher output capacity than the non-sterilized cells. The sterilized cells had an average output capacity of 2.82 ampere hours while the non-sterilized showed an average output capacity of 1.12 ampere hours. This difference could be attributed to the fact that the plate testing of Phase II (failure analysis) was carried out in flooded condition and with new separator material while all other capacities (Phase I, etc.) were measured with the cells intact.

6) One cell, S/N 3022 which had been heat sterilized and subjected to life cycling only during Phase I and Phase III testing, did not accept a charge during the plate testing of Phase II testing. The potentials measured between the reference electrode (Hg/HgO) and nickel plate, and between the reference electrode and the cadmium plate showed the latter to be normal (approximately -0.9 volts) and the former to be reversed (the polarity had reversed from +0.4 volt to approximately -0.9 volt) when compared to the other plate capacity measurements made during the Phase II testing using the same type reference electrode. The nickel lead of this cell was almost completely severed at its intersection with the electrode and had to be resoldered prior to making plate capacity tests.

1.0 Continued

The spectrographic and x-ray analysis of the residues filtered from the leach and plate testing solutions of cell S/N 3022 (which would not accept a charge during plate testing) revealed mainly cadmium hydroxide, cadmium carbonate and nickel metal. This cell had been sterilized and the chemical analysis of the electrolyte showed a carbonate content of 3.21 g. The carbonate content found in the electrolyte and that found in the residues from the leach and plate testing solution as cadmium carbonate might have contributed to this cell's inability to accept a charge. The nickel electrical lead which was almost severed from the electrode had to be re-soldered prior to making the plate capacity test, and this solder joint could have been an inferior joint electrically. However, an inferior solder joint could not account for the results obtained.

An emission spectrographic analysis of residues from the electrolyte leach operation and from the plate testing process for this cell showed the major metallic components to be nickel and cadmium, which would be expected even in a normal cell. An x-ray diffraction of the combined residues showed the major component to be cadmium hydroxide $Cd(OH)_2$. Also found to be present in intermediate concentrations were cadmium carbonate $CaCO_3$ and nickel (Ni). Although the spectrographic and x-ray analysis did show the presence of cadmium carbonate and because its effect on cell performance is not fully understood, these tests did not produce any conclusive evidence as to the cause of cell failure. However, cadmium carbonate could have contributed to the cell failure.

7) AC impedance measurements showed a wide spread from 12.5 to 900 millohms. The average impedance for the sterilized cells was 48 milliohms while the non-sterilized cells exhibited an average impedance of 247 milliohm. Although all the separators, except those from cells sterilized in the charged state, by visual inspection appeared to be uniformly wetted with electrolyte, it is possible that non-uniform distribution of the electrolyte in the separators and/or in the electrodes resulted in the observed high impedances.

8) Tensile strength measurements showed that in every case the separators from sterilized cells had lower tensile values than separators from non-sterilized cells. The average tensile strength of test samples cut parallel to the long axis of the separator for sterilized cells was 3.72 Kg. while comparable samples from non-sterilized cells was 5.44 Kg.. The average tensile strength of test samples cut perpendicular to the long axis of the separator for sterilized cells was 2.96 Kg. and for comparable samples of non-sterilized cells the value was 4.39 Kg.. There was also a slight variation in tensile strength (approximately 1.27 Kg.) of the same size test sample for any given separator indicating the possibility of a non-uniform separator.

1.0 Continued

9) Dimensional measurements of the separator showed that the width of separators from sterilized cells was approximately 1/32 inch less than that of separators from non-sterilized cells. The average thickness of separators from sterilized cells was 0.0122 inch, while separators from non-sterilized cells exhibited an average thickness of 0.0101 inch. In addition, the average variation in separator thickness for sterilized cells was about 2×10^{-3} inch and 20% less for non-sterilized, indicating a greater degree of non-uniformity in separators from sterilized cells.

2.0 INTRODUCTION

The purpose of this report is to present the results of the Failure Analysis Phase of a Heat Sterilizable Nickel-Cadmium Cell Test Program performed for the Jet Propulsion Laboratory, California Institute of Technology, under JPL Contract 951092 sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100. This program effort examined the failure mode analysis for control and heat sterilized cells subjected to 100% depth of discharge cycling.

Tests discussed in the following sections were performed on seventeen 4.0 ampere-hour, "D" size Sonotone nickel-cadmium cells. Twelve of these cells were selected from sixty cells which had been subjected to Phase I (1) testing. Two cells were selected from 31 cells which had been subjected to Phase I and Phase III (2) testing. Two (2) cells were control cells which had not been subjected to sterilization or any of the above test procedures. These cells were stored by JPL for approximately one (1) year prior to failure analysis. One cell was stored at 32°F and the other cell at 78°F. The final cell subjected to failure analysis testing was a special cell having the following history. This cell was manufactured by Sonotone to JPL instructions. The cell was not formed at the time of manufacture, and the plates were not matched. The unformed cell was stored for one month, after which the cell was heat sterilized and formed by JPL. After formation, the cell was subjected to fifteen (15) cycles and was stored for three months in the discharged open circuit condition prior to failure analysis.

The failure analysis tests consisted of: AC impedance, visual inspection, separator tensile strength, separator resistivity, separator dimensional check, electrolyte chemical analysis, and electrode capacity testing. The tests were designed to determine the contribution, if any, of the various cell components (separator, electrolyte and plates) to cell failure, and to compare test data of failed cells with non-failed cells. The tests were performed in accordance with the procedures discussed in the following sections relating to separator electrolyte and plate testing.

(1) Phase I - Testing as outlined in JPL's "Nickel-Cadmium Cell Test Statement of Work" dated February 10, 1965 and TRW Systems Test Procedure 9363.4-343, entitled "Heat Sterilization Testing of Nickel-Cadmium Cells", dated April 28, 1965.

(2) Phase II - Test Program as outlined in JPL's "Nickel-Cadmium Cell Test Statement of Work", dated August 30, 1966, and TRW Systems Test Plan, entitled "Heat Sterilizable Cell Characterization Test", dated November 2, 1966.

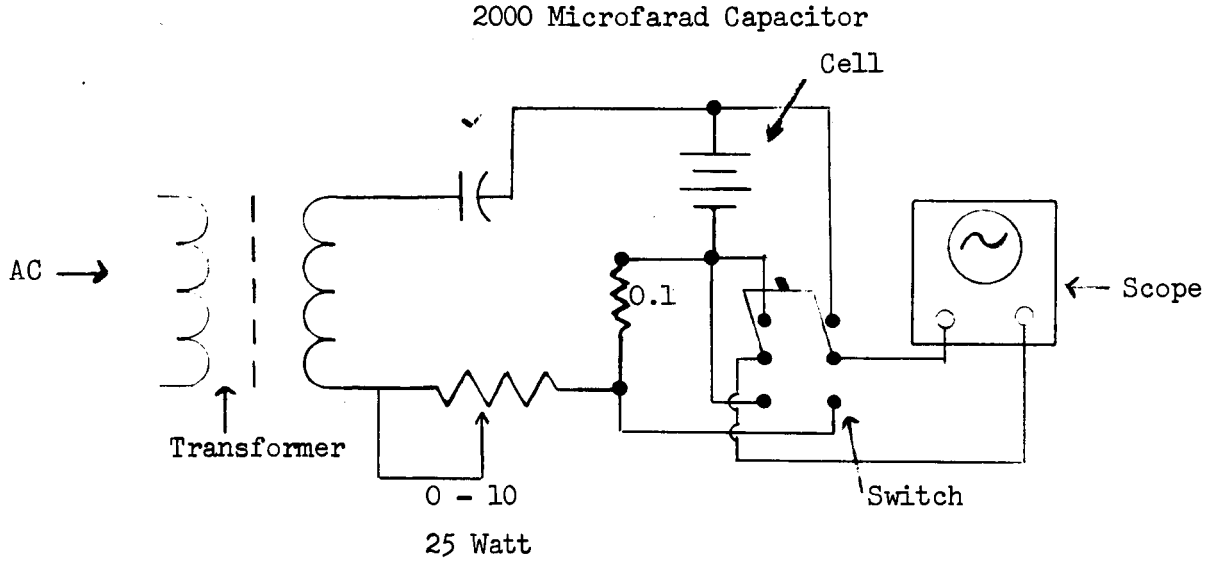
3.0 TEST METHODS AND RESULTS

3.1 Impedance Test

Prior to opening the cells for failure analysis, an AC impedance test was made on each cell. The AC bridge was of TRW design and the measurements were made at 60 Hz. Figure 1 is a diagram of the apparatus used for this test. The impedance measurements are in addition to the tests called out in the work statement of the contract. The results of the test are presented in Table I. Those cells having an impedance over 100 millohms showed no output capacity when checked just prior to cutting the cells open for failure analysis. Cells which had been sterilized and then placed on open circuit or float charge for varying lengths of time prior to life cycling during Phase I had higher input and output capacities (average input 4.32 ampere hours, average output 2.58 ampere hours) just prior to cutting the cells open for failure analysis than comparable cells which had not been sterilized (average input 0.04 ampere hours, average output 0.0 ampere hours). From the data presented in Table I, the average value of the measured impedance was calculated to be 27 milliohms for cells which had been sterilized and placed on open circuit or float charge stand prior to life cycling, while comparable cells which had not been sterilized had an average value of 306 milliohms. The average impedance value of sterilized cells regardless of test sequence of Phase I was 48 milliohms and 247 for non-sterilized cells. A comparison of sterilized cells with the control shows the impedance value of the control to be about 13 milliohms vs 48 milliohms for the sterilized. Possible drying or non-uniform distribution of the electrolyte in the separator and/or electrodes resulted in the observed higher impedances and the noted variations of the measured impedance.

3.2 Visual Observations

3.2.1 Cell Case, Leads, and Insulator. All cells tested during the failure analysis program showed the same general appearance regardless of whether or not the cell had been subjected to sterilization. The leads showed no signs of discoloration or corrosion. There was also no evidence of corrosion of the solder connection of the lead to the electrode tab. The inside of both the cell top and bottom for all cells showed a black discoloration. The nature of this discoloration was not determined. The inside of the walls of the cell case above the electrode-separator assembly also exhibited this black discoloration. The plastic insulators which were between the electrode-separator assembly and the wall of the cell case, and those which were on the top (3 insulators) and bottom (1 insulator) of the electrode-separator assembly showed no signs of degradation. There was no crazing, emrittlement or discoloration of the insulators. In general, there was little or no difference in the physical appearance of insulators between cells which had not been sterilized and those which had.



Test Apparatus for A.C. Impedance Measurements

Figure 1

TABLE I

Data Summary Failure Analysis

Cell No.	Sterilized	State of Charge at Sterilization	Test Parameter	Stand Time Days*	Impedance (Milliohms)	Cell Capacity at Start of Failure Analysis Input (A-H)	Cell Capacity at Start of Failure Analysis Output (A-H)	Electrolyte Analysis KOH (gm)	Electrolyte Analysis K_2CO_3 (gm)	Separator Tensile Strength (Kg) T_1	T_2	T_3	T_4	T_5	T_6	Separator Resistivity (Ohm-cm^2) R_1	R_2	R_3	Plate Capacity (A-H) Input	Plate Capacity (A-H) Output
2978	Control	---	1 year storage at 32°F	365	---	5.53	4.20	0.31	1.28	4.30	4.74	5.45	3.60	3.65	4.03	190	73	244	5.02	4.17
2958	Control	---	1 year storage at 78°F	365	12.5	4.23	3.67	1.815	3.141	4.32	4.46	5.50	4.52	3.80	5.80	455	500	433	6.66	4.33
3046	Yes	30%	Cycle life	300	300	0	0	2.44	2.43	2.96	3.93	2.40	2.66	3.54	3.30	149	312	272	6.48	4.60
3038	Yes	70%	Cycle life	300	95	0.54	0	1.27	2.88	---	---	---	---	---	---	---	---	---	6.60	4.43
3028	Yes	100%	Cycle life	300	33.8	2.24	0	1.02	4.09	---	---	---	---	---	---	---	---	---	6.60	3.99
3027	Yes	0%	Cycle life	32	17.5	7.13	3.60	1.72	2.44	2.69	3.64	3.90	2.65	2.66	3.35	202	342	776	6.11	4.29
2970	No	0%	Float 19 days, cycle life	45	67.5	0.04	0	1.48	1.33	4.83	4.58	5.06	4.41	3.77	4.44	1002	540	273	6.60	4.59
2971	Yes	0%	Float 19 days, cycle life	35	16.3	5.08	3.07	1.96	1.64	2.48	2.80	3.87	2.80	2.51	2.73	4407	166	5403	6.80	3.23
2994	No	0%	Open circuit 19 days, cycle life	51	237.5	0.08	0	1.66	1.49	4.80	5.95	5.00	4.74	4.96	4.79	423	269	523	6.80	4.79
2996	Yes	0%	Open circuit 19 days, cycle life	51	32.5	4.33	3.23	2.29	3.11	3.25	3.45	3.38	3.06	3.36	3.43	141	207	339	6.80	3.93
2985	No	0%	Float 230 days, cycle life	54	17.5	0.01	0	3.18	2.67	5.60	5.27	5.90	4.35	2.70	4.57	127	237	199	6.80	4.56
2986	Yes	0%	Float 230 days, cycle life	54	37.5	0.01	0	1.39	3.11	3.53	3.02	3.87	2.76	2.70	3.21	196	65	223	6.80	4.31
3008	No	0%	Open circuit 230 days, cycle life	55	900	0	0	2.40	3.17	5.90	6.13	6.84	4.45	4.80	3.80	144	197	404	6.80	4.72
3012	Yes	0%	Open circuit 230 days, cycle life	57	16.0	7.85	4.00	2.10	3.21	3.62	3.18	3.03	2.90	2.61	2.21	212	99	126	6.80	4.40
3017	No	0%	Cycle life - Phase I Cycle life - Phase III	--	250	1.67	0	2.253	3.148	5.80	6.66	7.00	5.27	5.28	4.45	124	197	253	6.80	5.06
3022	Yes	0%	Cycle life - Phase I Cycle life - Phase III	--	200	3.14	3.24	2.118	3.207	7.62	8.00	8.10	8.02	4.53	4.10	130	198	192	(a)	
2732[b]	Yes	Unformed			21.3	6.31	3.63	2.754	1.561	3.01	4.23	4.44	1.73	2.50	2.77	121	122	88	6.80	3.55

(a) Cell would not accept charge.

(b) Cell manufactured with unmatched plates and was not formed at time of manufacture. After approximately one year, the cell was sterilized then formed by JPL. After formation, the cell was cycled 15 times prior to failure analysis.

3.2.2 Separators. The separators in the control cells showed no signs of physical degradation. They were white in color, were easily removed from the electrode-separator assembly, and they were quite flexible. The separators from the cells which had been subjected to either a float or open circuit condition for varying lengths of time then placed on life cycle test all showed signs of degradation. Some of these cells had been heat sterilized and some had not. All of the separators from these cells were stuck to the electrodes in numerous places. This adherence was varied in the degree but was continuous along the length of the electrodes. Also, it was noted that both sides of the separators in these cells were black in color. It is presumed the black color was active material from both electrodes either imbedded or stuck to the separator surfaces. This deposition of active materials on the separator surfaces was not uniform as shown by variations in the black color. In a number of separators, it appeared that in some spots, the black deposits had penetrated completely through the separator. These spots were viewed through a binocular microscope but complete penetration of black deposits through the separator could not be confirmed. All separators in these cells showed some degree of warping.

The separator in the cells which were sterilized at 70% and 100% charge were severely degraded. The separator from the 70% charged cell had some degree of continuity but that from the 100% charged cell was discontinuous. The separator material in these cells was very brittle and flaky. The separator in the 30% charged cell was continuous but showed evidence of degradation in that it was warped and more brittle than the separator in the control cell.

The visual inspection of the separators from the cells tested during the failure analysis program showed that all the separators except those from the control cells were degraded to some degree regardless of the pre-failure analysis test condition. Except for cells which had been sterilized in the partially or fully charged state (which showed a high degree of separator degradation) there was little or no visual difference between the separators from cells which had been sterilized and those which had not.

Figures 2, 4, 6, and 8 show photographs of the separator-electrode assemblies as they were when removed from the case for cells S/N 2958 (control), 2985 (no sterilization, float 230 days, life cycled), 2986 (sterilized, float 230 days, life cycled) and 3028 (sterilized at 100% charge, life cycled) respectively. Note the adherence of fibrous separator material to the electrodes for those cells float charged for 230 days, then life cycled for both the sterilized and non-sterilized cells (Figures 4 and 6). This was noted on all cells except the control cell (Figure 2) in which there was no adhering separator material, and the cells which were sterilized in the partially or fully charged state (Figure 8) where the separator was partially destroyed.

3.2.2 Continued

Figures 3, 5, 7, and 9 show the separators from cells S/N 2958, 2985, 2986, and 3028. Note the dark spots (Figures 5 and 7) (presumed to be adherence of active electrode material to separator) on the separators from the cells which had been float charged for 230 days, then life cycled for both sterilized and non-sterilized cells. These dark spots were noted on the separators from all the cells except the control cell (Figure 3) and those cells sterilized in the partially or fully charged state (Figure 9). For these latter cells, frements of the separator were found adhering to the electrode surface as seen in Figure 9.

3.3 Separator Testing

The separators from cells selected for failure analysis were subjected to tensile strength, resistivity, and dimensional testing to determine, if any, the effect of heat sterilization on separator characteristics. The results of these tests are described below.

3.3.1 Tensile Strength of Separator. The tensile tests were made on a Hunter Tester Model TT-H. The grips of the tester were of TRW design. Because some potassium hydroxide (KOH) was still present in the separator, 100 grit sandpaper was affixed to the grip surfaces to prevent slippage. The test speed, that is, the rate of travel of the non-stationary grip was four inches per minute in all tests. The distance between the grips was 1 inch for the 1" x 3" test samples and 1/4 inch for the 1" x 2" test samples. The 1" x 3" test samples were cut along the longitudinal axis of the separator and the 1" x 2" samples were cut at right angles to the longitudinal axis of the separator. Three samples of each size were tested and they were cut from each separator at specified positions so a comparison between separators could be made. The selected positions were chosen so variations within any one separator could be observed. The relative positions of the test sample (T_1 ----- T_6) in relation to the complete separator are shown in Figure 10. The results of the testing are presented in Table 1.

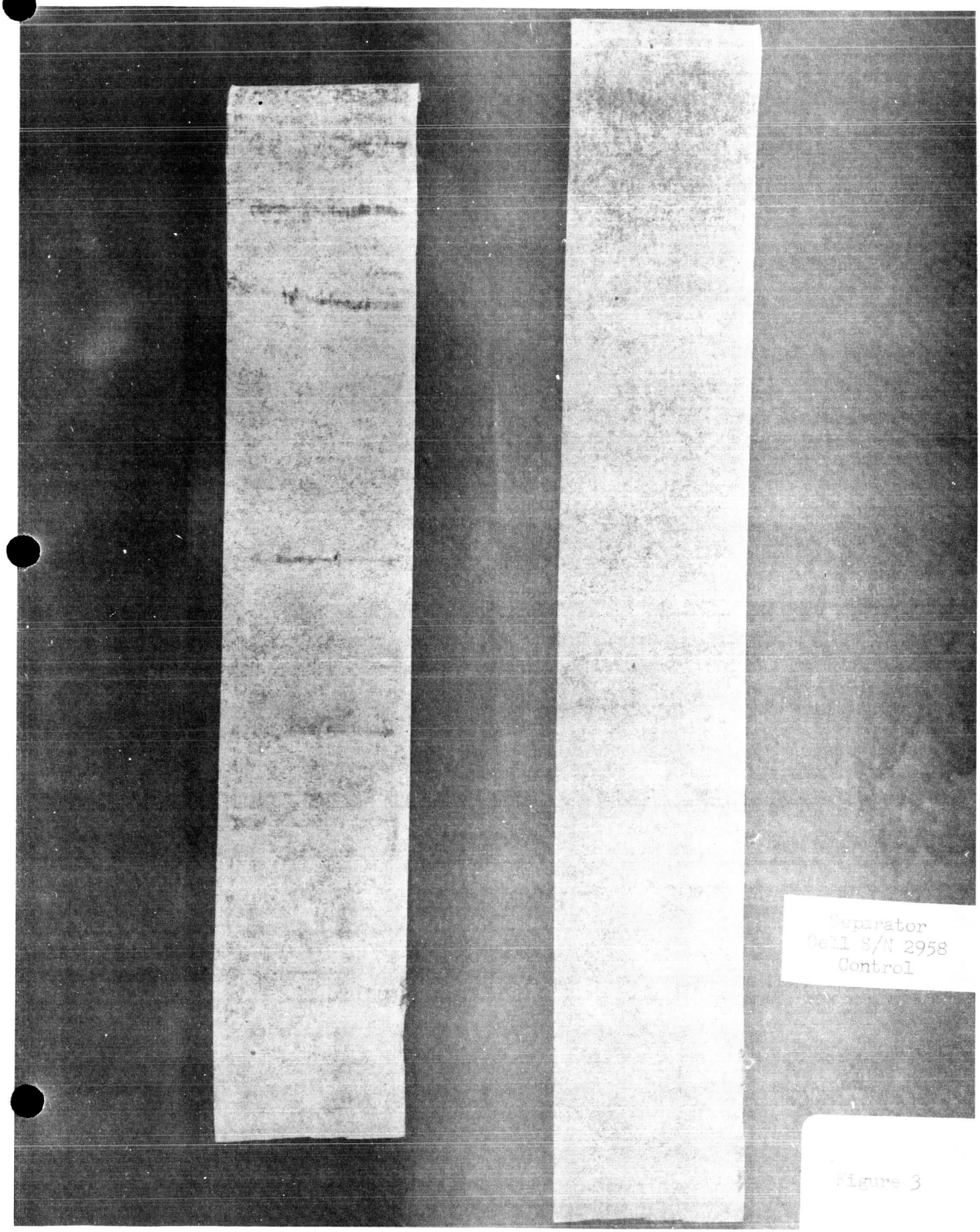
An analysis of the data shows the following:

1) In all cases, the tensile strength of separators in cells which had been subjected to the heat sterilization treatment were lower than those which were not heat sterilized.

2) There was a slight variation (approximately 1.27 Kg.) in the tensile strength of the same size test sample for any given separator indicating the possibility of a non-uniform separator.

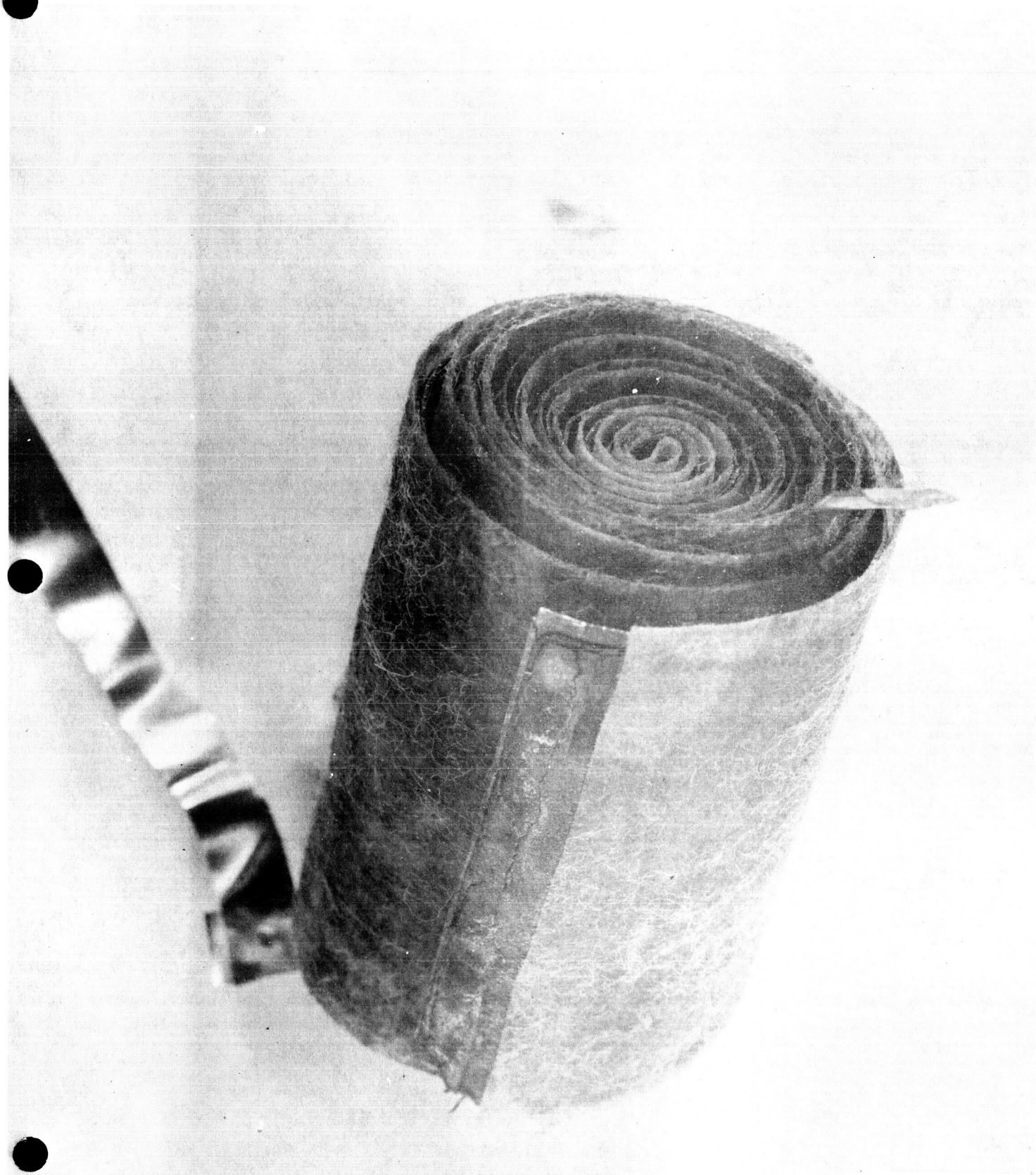
Separator-Electrode Assembly
Cell S/N 2958
Control

Figure 2



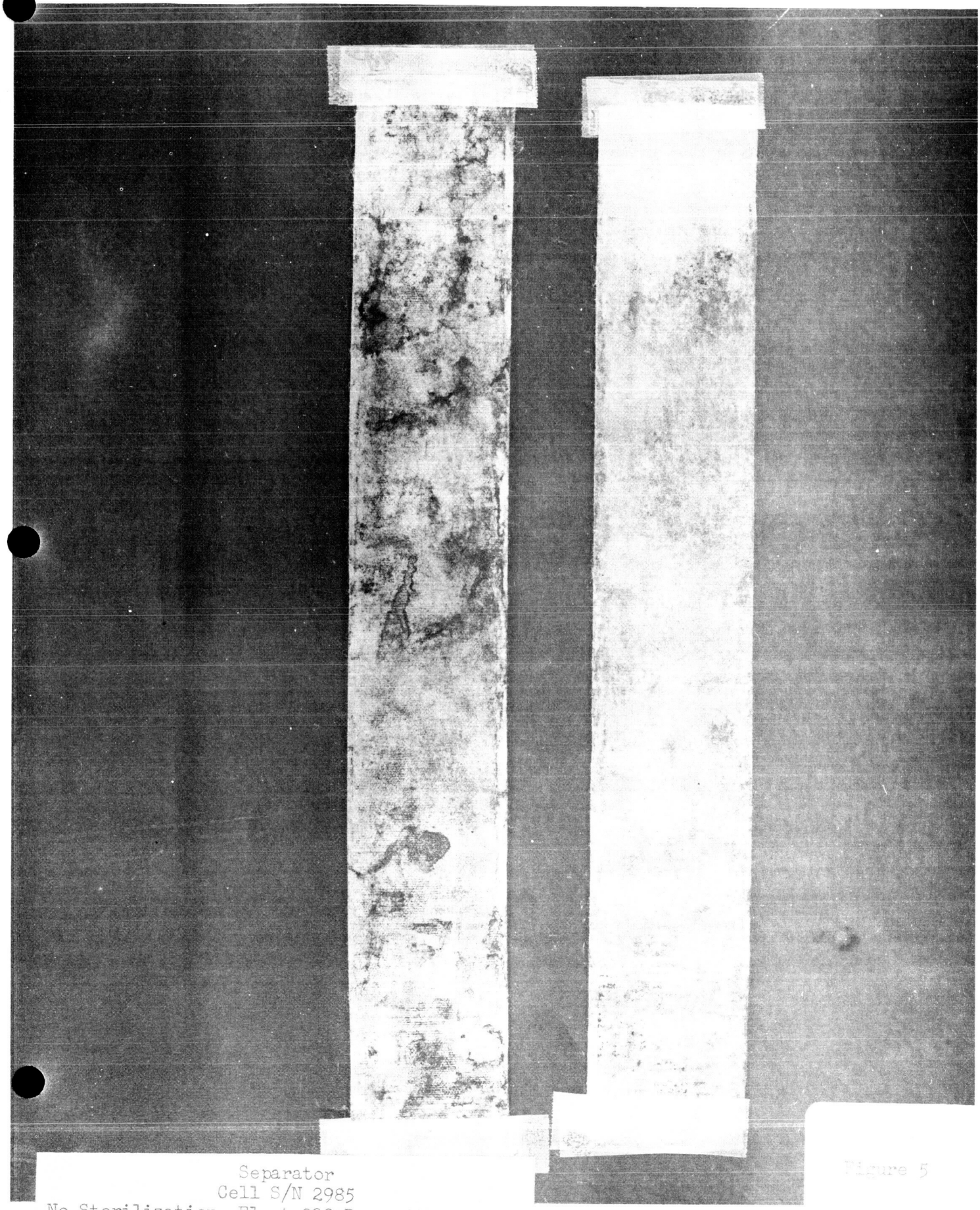
Separator
Cell S/N 2958
Control

Figure 3



Separator Electrode Assembly
Cell S/N 2985
No Sterilization, Float 230 Days, Life Cycled

Figure 4

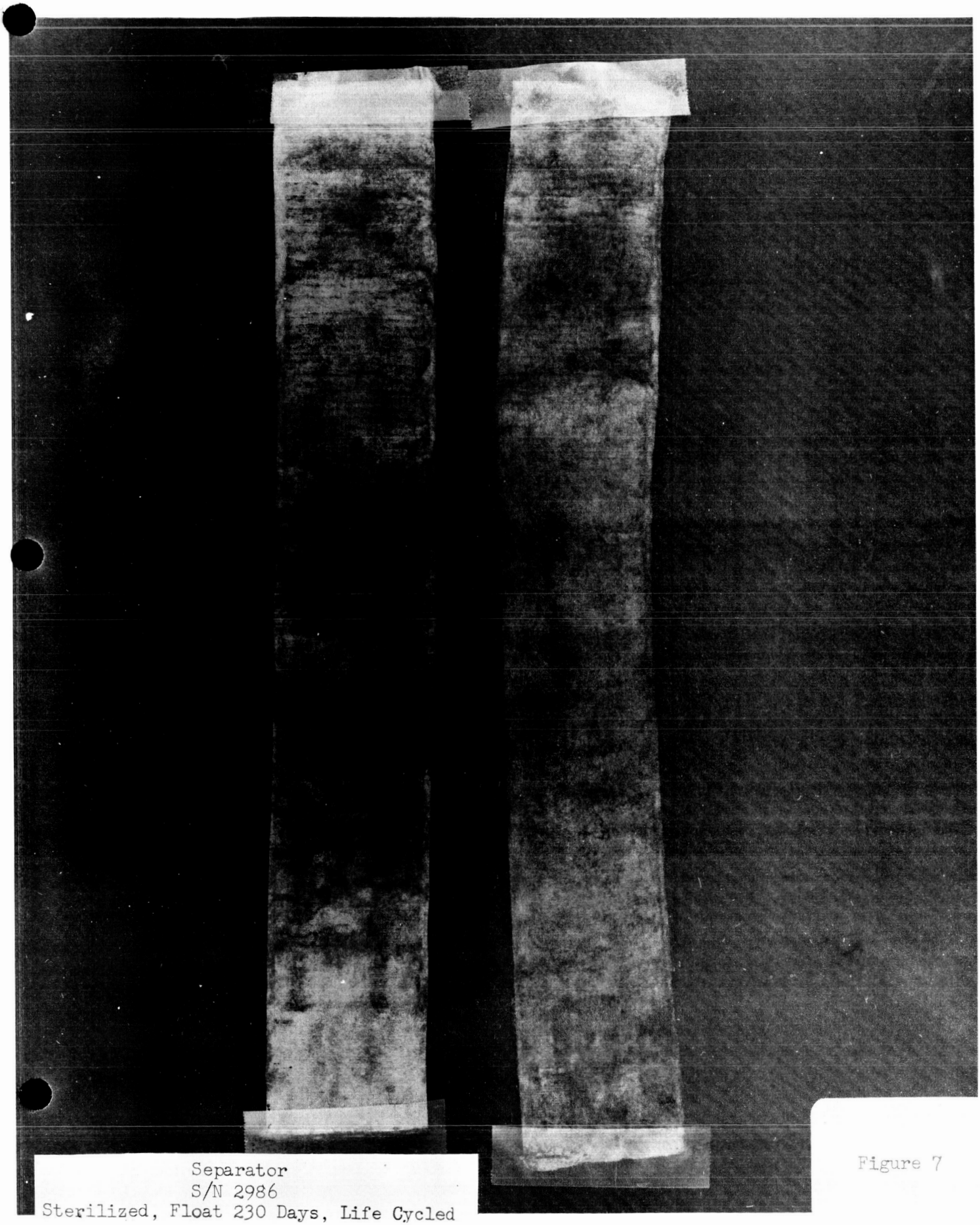


Separator
Cell S/N 2985
No Sterilization, Float 230 Days, Life Cycled

Figure 5

Separator Electrode Assembly
S/N 2986
Sterilized, Float 230 Days, Life Cycled

Figure 6

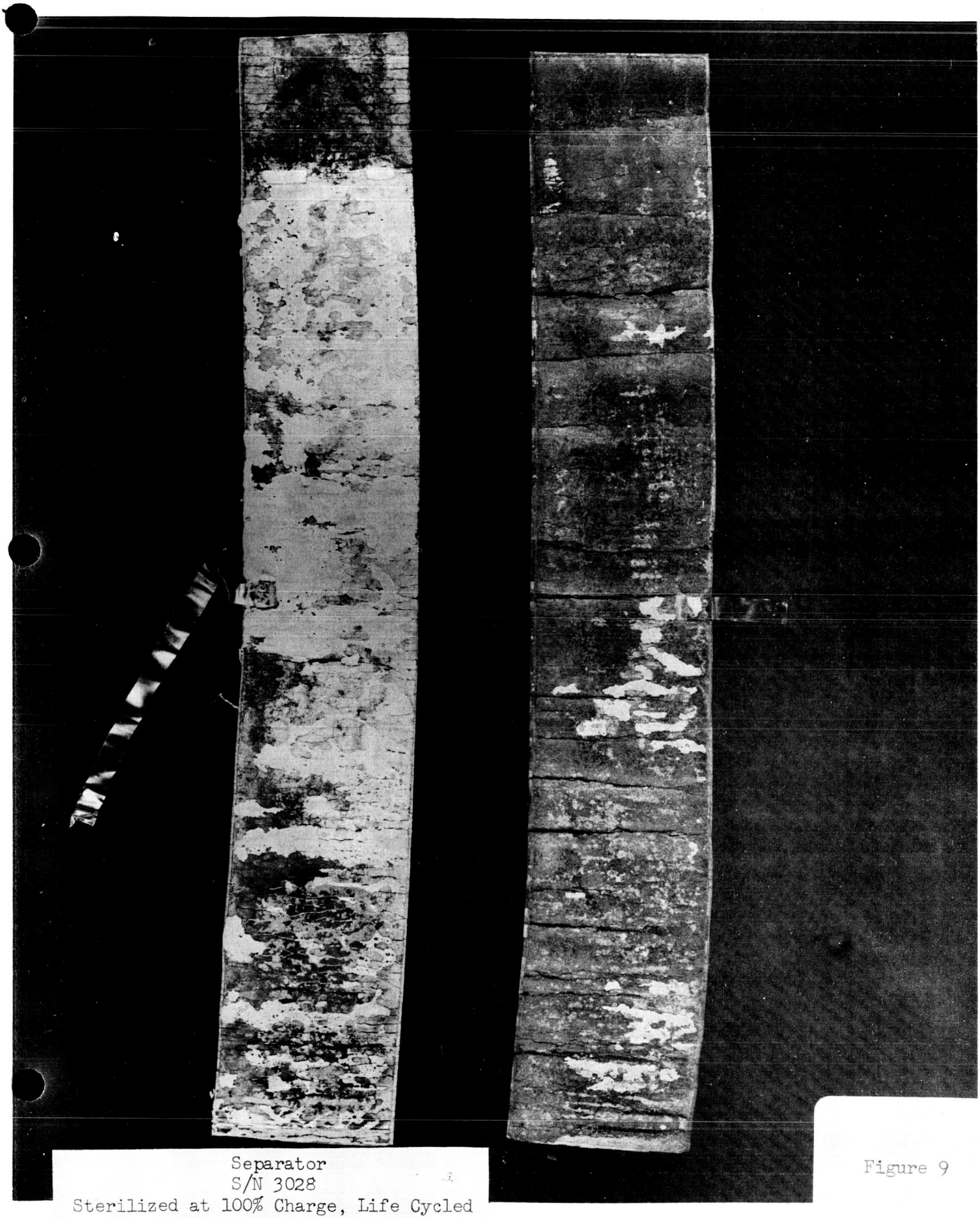


Separator
S/N 2986
Sterilized, Float 230 Days, Life Cycled

Figure 7

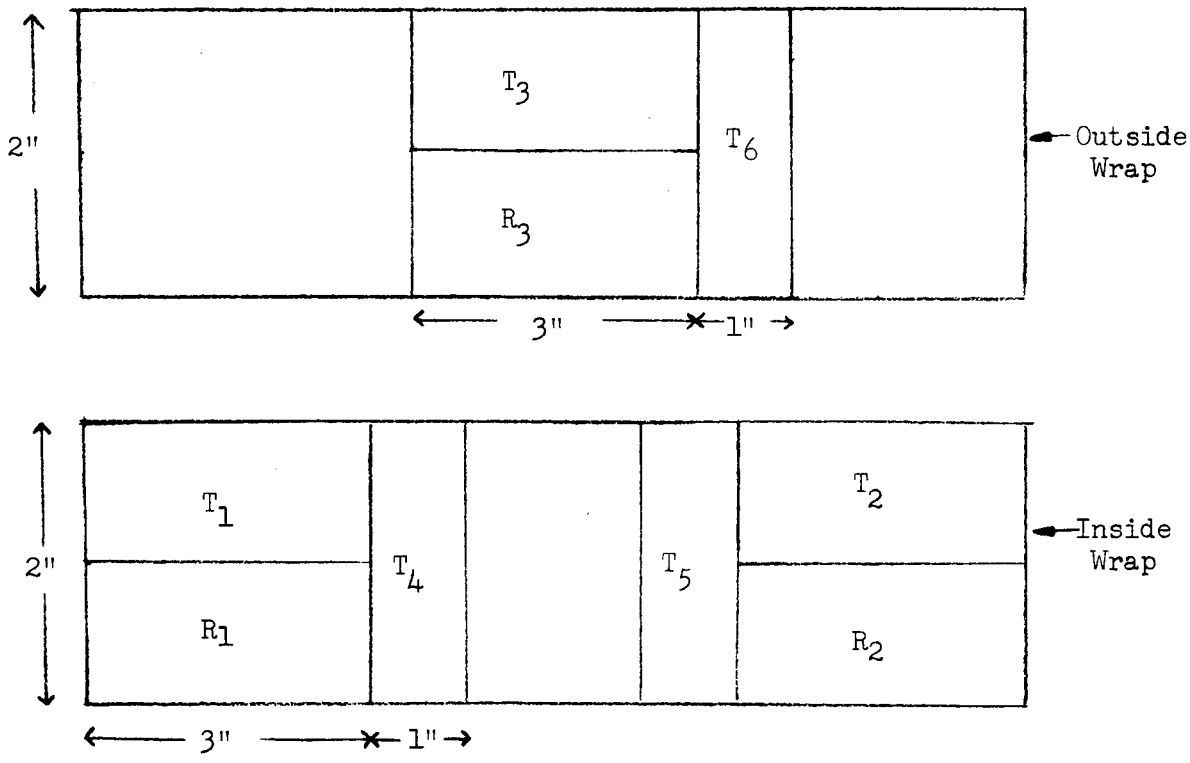
Separator Electrode Assembly
S/N 3028
Sterilized at 100% Charge, Life Cycled

Figure 8



Separator
S/N 3028
Sterilized at 100% Charge, Life Cycled

Figure 9



Relative Position of Separator Resistivity and Tensile Samples

FIGURE 10

Legend

R - Resistivity samples
T - Tensile samples

3.3.1 Continued

3) In general, the smaller size test samples (T_4, T_5, and T_6 in Table I) had on the average a 20% lower tensile strength than the larger test samples (T_1, T_2, and T_3 in Table I) from the same separator. This could be attributed to the fact that the different size test samples were cut from the separator at right angles to one another and might be a function of the grain of the separator, or it could be a function of the distance between the grips described above.

3.3.2 Resistivity of Separator. The resistivity testing was made using an apparatus similar to that shown on page 55 of "Battery Separator Screening Methods" by Cooper and Fleischer. A direct current method was used. Mercury/mercury oxide electrodes were used as the reference electrodes and partially charged cadmium plates were used as the working electrodes. The surface area of the separator exposed in the test apparatus was 1.27 cm^2. The testing was conducted in a CO_2 free enclosure and the electrolyte used in the test apparatus was 1.3 Sp. Gr. KOH prepared using CO_2 free distilled water. Three samples of each separator were subjected to resistivity testing. As was the case for the tensile test, the test samples were taken from specified position of each separator so a comparison between separators could be made. Three samples were taken from each separator to determine the variation of resistivity within any one separator. The relative position of the test samples (R_1 --- R_3) in relation to the complete separator are shown in Figure 10. As can be seen from Figure 10, all resistivity samples were cut along the longitudinal axis of the separator. The data for the resistivity testing are presented in Table 1.

As can be seen from the data, there is a considerable variation in the resistivity measurement for any one separator. Also, there is no correlation between the measured resistivities and sterilization, that is, the separators from cells which had been sterilized showed resistivities both higher and lower than those from non-sterilized cells. The irregularities or variations noted in the resistivity measurements could be attributed to the following:

1) Non-uniform thickness of separator caused by its varied degree of adherence along the electrode surfaces. The non-uniformity in thickness was confirmed by thickness measurements made on the resistivity samples which are presented in the following section.

3.3.2 Continued

2) Non-uniform deposition of active electrode materials on the separator surfaces. This non-uniform deposition was discussed in the section on visual observation of separator of this report.

3.3.3 Dimensional Measurement of Separator. In addition to the tests called out in the work statement, measurements were made of the separator thickness and width. Thickness was measured by placing the separator between two pieces of glass microscope slide and measuring the thickness of this assembly with a micrometer. The separator thickness was obtained by subtracting the thickness of the two pieces of glass microscope slide. Each sample was measured in three different places. The pieces of microscope slide measured one inch by 1-7/16 inch. Thickness measurements were made on each of the samples cut from the separators for the resistivity testing (R_1, R_2, R_3 in Table 2) and the portions of the separator not subjected to any testing (outer and inner wrap in Table 2). The area covered by the microscope slide on the outside and inside separator wrap covered by the glass microscope slide was 1.44 sq. inches. The separator width was measured using a metal ruler graduated in 1/32 of an inch. No width measurements were made on the resistivity samples as they were cut along the length of the separator. The data for the separator thickness and width are given in Table II and Table III respectively. Figure 11 is a plot of the average thickness of the resistivity samples versus resistivity. As can be seen from the plot, there is a considerable spread, and there seems to be no correlation between separator thickness and resistivity. However, the plot of variation in thickness of resistivity samples versus cell number (Figure 12) shows a greater spread in thickness and greater thicknesses for separators of cells which had been subjected to heat sterilization. As mentioned previously, this larger and higher spread in separator thickness is not reflected by the resistivity measurements. However, the effect of variation of thickness could possibly be masked by the effect of adherence of active electrode materials to the separator surface.

3.4 Electrolyte Chemical Analysis

The leaching of the electrolyte (1.3 Sp. Gr. KOH) from the separator-electrode assemblies was done in a carbon dioxide (CO_2)-free enclosure and the leach solution used was boiled, CO_2-free, water. These precautions were necessary as the leach solution was subsequently analyzed for carbonate ($CO_3^{=}$), and hydroxide (OH^-) content. Any CO_2 present during the leaching process would have reacted with cell electrolyte forming carbonate which would have given erroneous results. Several methods for leaching the electrolyte (which would account for some variation in the data) were tried. The method found to be most satisfactory was as follows:

TABLE II

DATA SUMMARY OF SEPARATOR THICKNESS

Cell No.	Sample	Measured Thickness (Thousandth of Inch) 1	2	3	$\Delta T^{(a)}$	Average Thickness	Average Thickness R1+R2+R3	Remarks
2978	R_1	11.00	11.25	11.70	1.25	11.65		
	R_2	10.50	10.75	10.50	0.25	10.58	10.72	Control
	R_3	10,25	9.50	10.00	0.75	9.92		
2958	R_1	9.00	9.25	9.70	0.70	9.32		
	R_2	10.30	10.75	10.50	0.45	10.52	9.61	
	R_3	9.25	9.25	8.50	0.75	9.00		Control
	Inner Wrap	11.00	10.50	10.25	0.75	10.25		
	Outer Wrap (Large)	8.25	7.75	8.40	0.65	8.13		
	Outer Wrap (Small)	9.80	10.50	10.00	0.70	10.10		
3028	Separator destroyed by heat sterilization							
3038	Separator destroyed by heat sterilization							
3046	R_1	16.25	10.75	10.75	5.50	12.58		
	R_2	10.25	11.75	12.75	2.00	11.58	11.72	Heat sterilized at 40% charge,
	R_3	10.75	11.50	10.75	0.75	11.00		life test
	Inner Wrap	8.75	8.50	9.25	0.75	8.83		
	Outer Wrap (Large)	10.25	11.00	11.00	0.75	10.75		
	Outer Wrap (Small)	14.50	16.00	14.25	1.75	14.92		
3027	R_1	11.00	12.00	14.50	3.50	12.50		
	R_2	10.50	10.50	11.50	1.00	10.83	11.55	Heat sterilized at 0% charge,
	R_3	12.00	10.50	10.50	1.50	11.33		life test
	Inner Wrap	10.50	10.25	9.75	0.75	10.17		
	Outer Wrap (Large)	10.75	12.25	12.75	2.00	11.92		
	Outer Wrap (Small)	10.50	15.25	15.30	4.80	13.68		
2970	R_1	11.50	11.75	12.75	1.25	12.00		
	R_2	12.50	12.25	11.50	1.00	12.08	11.43	No sterilization, float
	R_3	10.50	10.00	10.00	0.50	10.17		19 days, life test
	Inner Wrap	12.25	11.75	11.75	0.50	11.92		
	Outer Wrap (Large)	11.50	12.50	14.75	3.25	12.92		
	Outer Wrap (Small)	12.50	11.75	11.75	0.75	12.00		

TABLE II

DATA SUMMARY OF SEPARATOR THICKNESS (Continued)

Cell No.	Sample	Measured Thickness (Thousandth of Inch) 1	2	3	ΔT[a]	Average Thickness	Average Thickness R1+R2+R3	Remarks
2971	R_1	11.50	12.50	14.50	3.00	12.83		
	R_2	15.40	11.50	11.50	3.90	12.80	12.65	Heat sterilized at 0% charge,
	R_3	11.50	12.75	12.75	1.25	12.33		float 19 days, life test
	Inner Wrap	11.75	12.25	11.75	0.50	11.92		
	Outer Wrap (Large)	12.25	12.25	14.50	2.25	13.00		
	Outer Wrap (Small)	13.25	18.40	17.70	5.15	16.45		
2994	R_1	10.00	9.75	10.50	0.75	10.08		
	R_2	9.75	9.75	10.00	0.25	9.98	9.91	No sterilization, open circuit
	R_3	10.25	9.50	9.30	0.95	9.68		19 days, life test
	Inner Wrap	11.50	11.50	11.50	0.0	11.50		
	Outer Wrap (Large)	10.00	11.25	11.25	2.25	11.17		
	Outer Wrap (Small)	10.25	11.25	10.75	1.00	10.75		
2996	R_1	13.00	14.30	15.00	2.00	14.10		
	R_2	12.00	11.40	13.50	1.50	12.30	12.59	Heat sterilized at 0% charge,
	R_3	10.70	11.75	11.70	1.05	11.38		open circuit 19 days, life test
	Inner Wrap	10.50	11.00	10.50	0.50	10.67		
	Outer Wrap (Large)	10.75	12.50	13.50	2.75	12.25		
	Outer Wrap (Small)	11.50	17.50	16.50	6.00	15.17		
2985	R_1	9.00	9.25	9.70	0.70	9.32		
	R_2	10.30	10.75	10.50	0.45	10.52	9.61	No sterilization, float 230 days,
	R_3	9.25	9.25	8.50	0.75	9.00		life test
	Inner Wrap	11.00	10.50	10.25	0.75	10.25		
	Outer Wrap (Large)	8.25	7.75	8.40	0.65	8.13		
	Outer Wrap (Small)	9.80	10.50	10.00	0.70	10.10		
2986	R_1	13.50	12.70	13.00	0.80	13.07		
	R_2	12.70	14.80	15.80	3.10	14.43	13.03	Heat sterilized at 0% charge,
	R_3	11.50	11.30	12.00	0.70	11.60		float 230 days, life test
	Inner Wrap	11.25	10.70	10.70	0.55	10.88		
	Outer Wrap (Large)	13.50	11.00	11.00	2.50	11.83		
	Outer Wrap (Small)	11.25	16.40	16.40	5.15	14.68		

TABLE II

DATA SUMMARY OF SEPARATOR THICKNESS (Continued)

Cell No.	Sample	Measured Thickness (Thousandth of Inch) 1	2	3	ΔT[a]	Average Thickness	Average Thickness R1+R2+R3	Remarks
3008	R_1	9.50	10.00	10.25	0.75	9.92	9.14	No sterilization, open circuit 230 days, life test
	R_2	8.75	8.75	8.75	0.00	8.75		
	R_3	8.75	8.75	8.75	0.00	8.75		
	Inner Wrap	9.25	9.50	9.00	0.50	9.25		
	Outer Wrap (Large)	9.25	9.50	10.00	0.75	9.58		
	Outer Wrap (Small)	8.75	9.75	8.50	1.25	9.00		
3012	R_1	13.50	11.75	11.25	2.25	12.17	11.58	Heat sterilized at 0% charge, open circuit 230 days, life test
	R_2	10.75	10.50	10.25	0.50	10.50		
	R_3	12.75	11.25	12.25	1.50	12.08		
	Inner Wrap	10.00	9.50	9.00	1.00	9.50		
	Outer Wrap (Large)	11.75	12.75	14.50	2.75	12.92		
	Outer Wrap (Small)	16.50	17.25	16.25	1.00	16.67		
3017	R_1	10.50	11.50	11.75	1.25	11.25	10.25	No sterilization, life cycled, characterization test
	R_2	9.75	10.25	9.25	1.00	9.75		
	R_3	10.75	9.25	9.25	1.50	9.75		
	Inner Wrap	10.75	13.00	10.25	2.75	11.33		
	Outer Wrap (Large)	10.25	9.25	9.00	1.25	9.83		
	Outer Wrap (Small)	8.75	9.75	9.25	1.00	9.42		
3022	R_1	12.25	11.75	12.75	1.00	12.25	11.72	Heat sterilized, life cycled, characterization test
	R_2	12.25	11.25	13.75	2.50	12.42		
	R_3	11.00	10.75	9.75	1.25	10.50		
	Inner Wrap	10.50	10.50	13.75	3.25	11.58		
	Outer Wrap (Large)	10.75	13.50	16.75	6.00	13.67		
	Outer Wrap (Small)	10.75	12.75	---	2.00	11.75		

TABLE 2

DATA SUMMARY OF SEPARATOR THICKNESS (Continued)

Cell No.	Sample	Measured Thickness (Thousandth of Inch) 1	2	3	T[a]	Average Thickness	Average Thickness R1+R2+R3	Remarks
2732	R_1	14.25	16.25	16.50	2.25	15.67	12.39	Special cell[b]
	R_2	10.50	10.50	11.25	0.75	10.83		
	R_3	11.00	9.75	11.25	1.25	10.67		
	Inner Wrap	11.25	13.00	16.25	1.75	11.83		
	Outer Wrap (Large)	11.25	11.25	8.75	2.50	10.42		
	Outer Wrap (Small)	9.25	9.25	9.75	0.25	9.42		

(a) Difference between maximum and minimum measured thickness.

(b) Cell manufactured with unmatched plates, was not formed at time of manufacture, and a vacuum fill technique was used for the addition of the electrolyte. After approximately 1 year cell was sterilized and formed by JPL. After formation, the cell was cycled 15 times prior to failure analysis.

TABLE III

DATA SUMMARY OF SEPARATOR WIDTH

Cell No.	Sample	Width Measured (Inches) 1	2	3	Average Width (In.)	Remarks
2978	Sample destroyed in tritration for KOH and K_2CO_3					Control
2958	Inner Wrap	2	2	2	2	
	Outer Wrap (Large)	2	2	2	2	Control
	Outer Wrap (Small)	2	2	2	2	
3028	Separator destroyed by heat sterilization					
3038	Separator destroyed by heat sterilization					
3046	Inner Wrap	1 31/32	1 31/32	1 31/32	1 31/32	Heat sterilized at 40%
	Outer Wrap (Large)	1 31/32	1 31/32	1 31/32	1 31/32	charge, life test
	Outer Wrap (Small)	1 31/32	1 30/32	1 30/32	1 61/64	
3027	Inner Wrap	2	1 31/32	1 31/32	1 63/64	Heat sterilized at 0%
	Outer Wrap (Large)	1 31/32	1 31/32	1 31/32	1 31/32	charge, life test
	Outer Wrap (Small)	1 31/32	1 31/32	1 31/32	1 31/32	
2970	Inner Wrap	2	2	2	2	No sterilization, float
	Outer Wrap (Large)	2	2	2	2	19 days, life test
	Outer Wrap (Small)	2	2	2	2	
2971	Inner Wrap	2	2	2	2	Heat sterilized at 0%
	Outer Wrap (Large)	1 31/32	1 31/32	1 31/32	1 31/32	charge, float 19 days,
	Outer Wrap (Small)	1 31/32	1 31/32	1 31/32	1 31/32	life test
2994	Inner Wrap	2	2	2	2	No sterilization, open
	Outer Wrap (Large)	1 31/32	1 31/32	2	1 63/64	circuit 19 days, life
	Outer Wrap (Small)	2	2	2	2	test
2996	Inner Wrap	1 31/32	1 31/32	1 31/32	1 31/32	Heat sterilized at 0%
	Outer Wrap (Large)	1 31/32	1 31/32	1 31/32	1 31/32	charge, open circuit
	Outer Wrap (Small)	1 31/32	1 31/32	1 31/32	1 31/32	19 days, life test
2985	Inner Wrap	2	2	2	2	No sterilization, float
	Outer Wrap (Large)	2	2	2	2	230 days, life test
	Outer Wrap (Small)	2	2	2	2	
2986	Inner Wrap	1 31/32	1 31/32	1 31/32	1 31/32	Heat sterilized at 0%
	Outer Wrap (Large)	1 31/32	1 31/32	1 31/32	1 31/32	charge, float 230 days,
	Outer Wrap (Small)	1 31/32	1 31/32	1 31/32	1 31/32	life test
3008	Inner Wrap	2	2 1/32	2 1/32	2 1/64	No sterilization, open
	Outer Wrap (Large)	2	2	2	2	circuit 230 days, life
	Outer Wrap (Small)	2	2	2	2	test
3012	Inner Wrap	1 31/32	1 31/32	1 31/32	1 31/32	Heat sterilized at 0%
	Outer Wrap (Large)	1 31/32	1 31/32	1 30/32	1 61/64	charge, open circuit
	Outer Wrap (Small)	1 30/32	1 30/32	1 30/32	1 30/32	230 days, life test

TABLE III

DATA SUMMARY OF SEPARATOR WIDTH (Continued)

Cell No.	Sample	Width Measured (Inches) 1	2	3	Average Width (In.)	Remarks
3017	Inner Wrap	2	2	2	2	No sterilization, life
	Outer Wrap (Large)	2	2	2	2	cycled, characterization
	Outer Wrap (Small)	2	2	2	2	test
3022	Inner Wrap	not enough to measure				Heat sterilized, life
	Outer Wrap (Large)	1 7/8	1 7/8	---	1 7/8	cycled, characterization
	Outer Wrap (Small)	1 7/8	1 7/8	1 7/8		test
2732	Inner Wrap	2	2	2	2	Special cell*
	Outer Wrap (Large)	2	2	2	2	
	Outer Wrap (Small)	2	2	2	2	

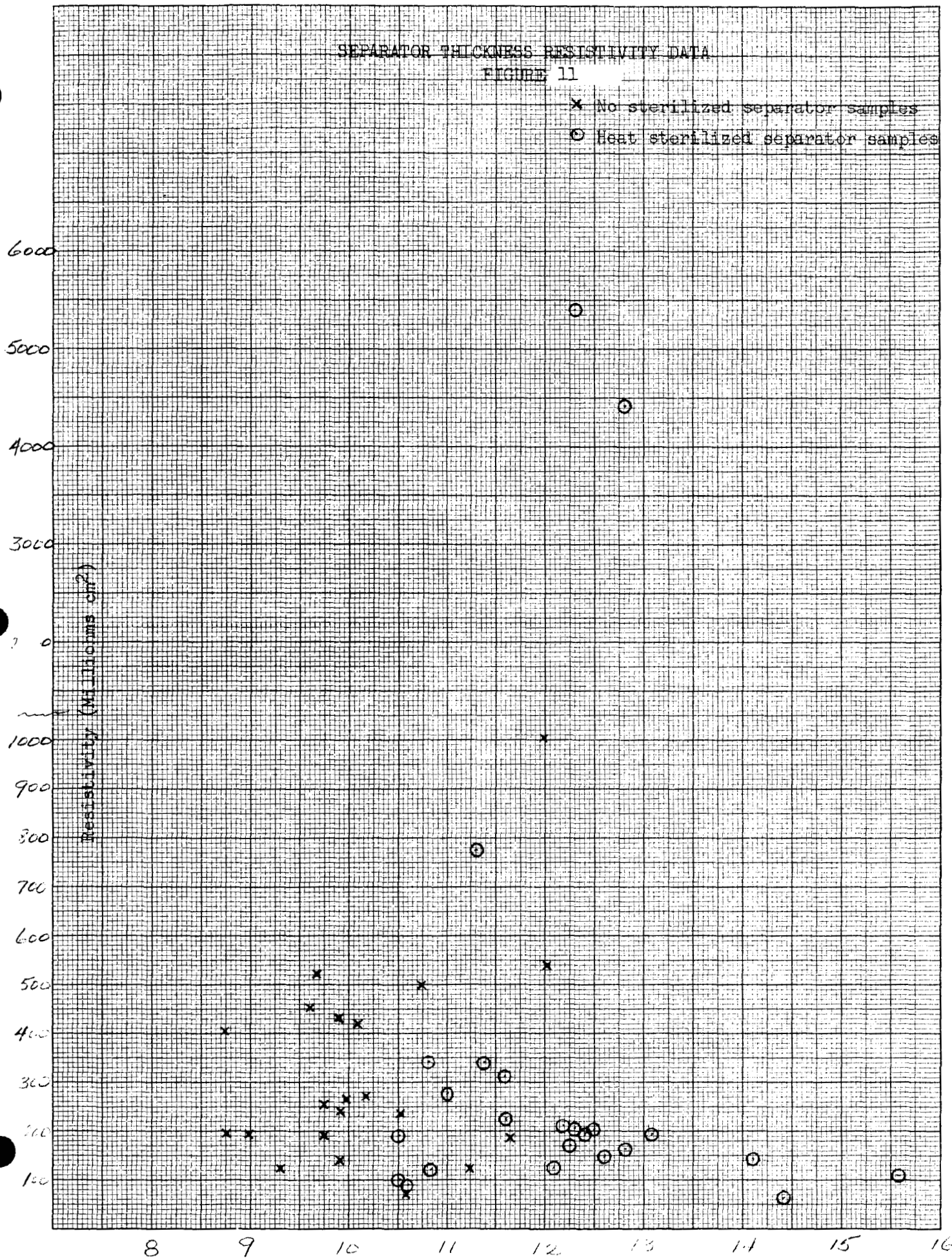
*Cell manufactured with unmatched plates, was not formed at time of manufacture, and a vacuum fill technique was used for the addition of the electrolyte. After approximately 1 year, cell was sterilized and formed by JPL. After formation, the cell was cycled 15 times prior to sterilization.

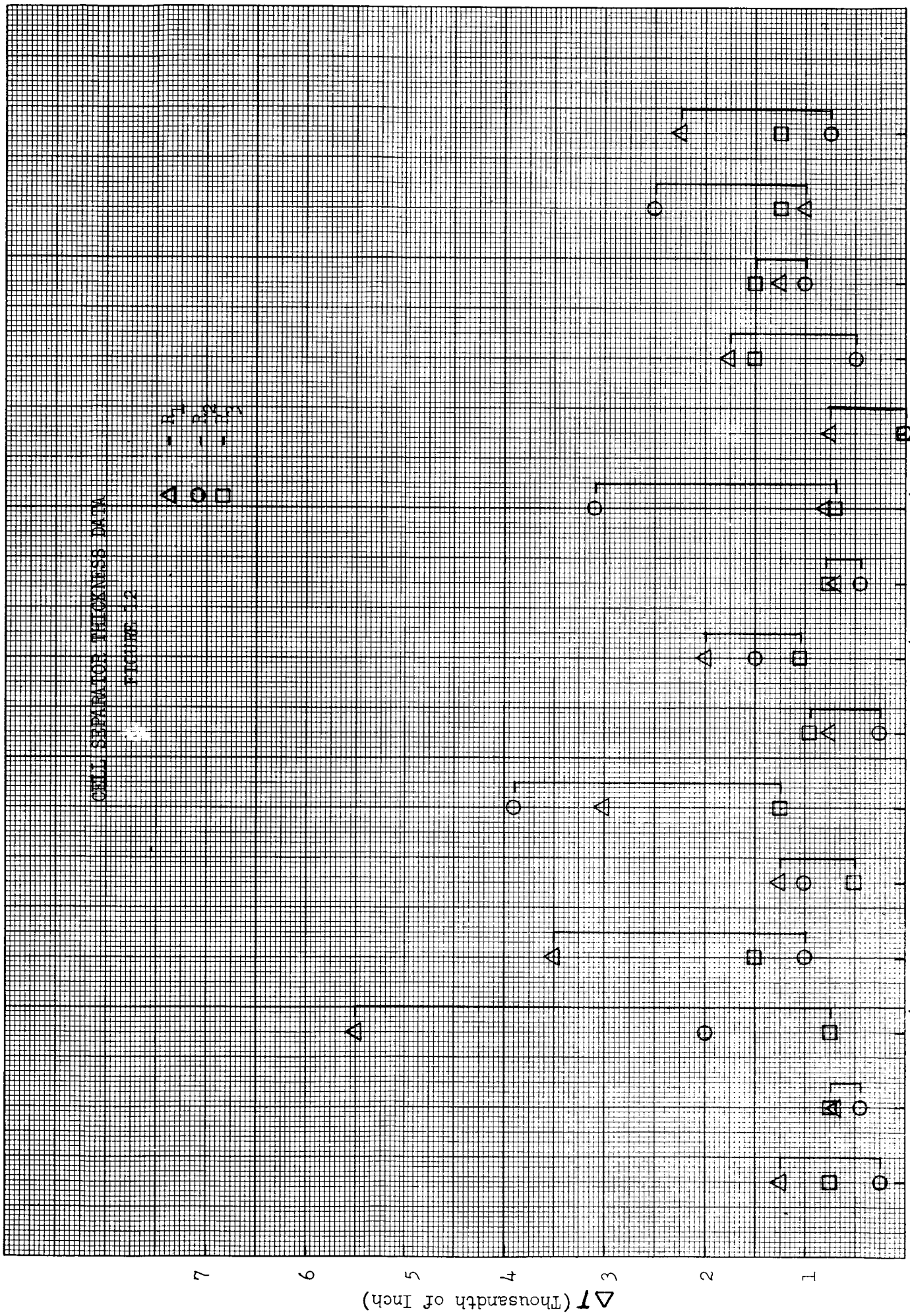
SEPARATOR THICKNESS RESISTIVITY DATA

FIGURE 11

× No sterilized separator samples

⊙ Heat sterilized separator samples




CELL SEPARATOR THICKNESS DATA
FIGURE 12
ΔT (Thousandth of Inch)
1
2
3
4
5
6
7
2798
2958
3046
3027
2970
2971
2944
2996
2985
2986
3008
3012
3017
3022
2732
Cell Serial Number

3.4 Continued

The cell with top and bottom removed was placed in an upright postion in a funnel, and approximately 300 cc of CO_2-free water was poured through it. The CO_2-free water containing any leached electrolyte was funnelled into a 400 cc beaker. The cell was then removed from the funnel and the side of the cell case cut open and the separator-electrode assembly removed. The assembly was then completely unwrapped, rewrapped in a loose configuration, and placed in the beaker containing the leach solution for 1 hour. The unwrapping and rewrapping of the separator-electrode assembly allowed better percolation of leach solution through the assembly. After 1 hour in the leach solution, the assembly was removed and placed in a 400 cc beaker containing approximately 300 cc of fresh CO_2-free water. The assembly was removed and the separator and plates subjected to their respective tests. The contents of the two beakers, each containing approximately 300 cc of leach solution, were diluted to 500 cc in volumetric flask and analyzed for KOH and K_2CO_3 using a method by Vogel (1).

The data for the analysis are presented in Table 1. As can be seen by the data, there is a variance between cells tested which could possibly be due to alterations made in the leaching process. What is noteworthy is the fact that all the cells showed a high concentration of carbonate relative to hydroxide. There was little difference in the carbonate content between cells which had been sterilized and those which had not. Also, the control cell (S/N 2958) which had not been sterilized but had been on open circuit stand for 1 year at 78°F showed a carbonate content comparable to cells which had been sterilized and subjected to the various tests of the cycle life program (Phase I). The cells which had failed during the cycle life program and subject to failure analysis program also showed comparable carbonate content. The results of this analysis show that there was little or no carbonate formation (resulting possibly from separator degradation) during sterilization because essentially the same amount was found in both sterilized and non-sterilized cells. The noted differences are probably a result of changes in the leaching process and experimental error.

There was considerable variation of the carbonate from cell to cell and no definite trend of the effect of carbonate could be established. A comparison of the carbonate content of only those cells which had been on open circuit or float charge prior to life cycling during Phase I, shows that cells subjected to heat sterilization had an average carbonate content of 2.52 g. while those not sterilized had 2.17 g. carbonate. The average plate capacity for these same cells was 3.96 ampere hours for those subjected to sterilization and 4.67 ampere hours for non-sterilized cells. Thus, a higher carbonate content was associated with a lower plate capacity. However,

(1) Vogel, Quantitative Inorganic Analysis, John Wiley and Sons, Inc., Third Edition, 1961, pages 249 - 251.

3.4 Continued

comparison of these same sterilized cells with the control cell S/N 2958 (control cell S/N 2978 is not considered because it was the first attempt at analyzing the electrolyte and the leach process was inadequate) shows the control cell has a carbonate content approximately 23% higher than the average of the sterilized, float-open circuit stand cells, and a plate capacity that was 9.3% higher. This indicates the opposite, or higher, carbonate content reflects itself in increasing the plate capacity. Comparison of the non-sterilized cells with the control again indicate the higher carbonate reflects itself in lowering the plate capacity. Although the carbonate content of the electrolyte undoubtedly had some effect on cell capacity and plate performance, the variation in carbonate content from cell to cell was wide and contradictory.

3.5 Electrodes - Plate Testing

After the separator was removed from the electrode-separator assembly for inspection and testing, another piece of separator material (Webril EM470) was inserted between the electrodes to provide physical separation of the plates in the spiral configuration. This assembly was put in a glass container and placed in the CO_2-free enclosure. A potassium hydroxide solution (prepared using CO_2-free distilled water) having a specific gravity of 1.296 at 26°C was poured into the jar so that it covered the electrode-separator assembly completely. A mercury/mercury oxide reference electrode was used so that the voltage of each electrode could be obtained during the charge and discharge cycle. The potential difference between the electrodes, that between the nickel and the reference electrode, that between the cadmium and the reference electrode and the current were recorded on a multipoint strip-chart recorder throughout the charge-discharge cycle. The cells were charged at a constant current of 400 ma for 16.5 hours (three cells, S/N's 2978, 3027 and 3046 were inadvertently stopped short of 16.5 hours charge time). They were discharged at a constant current of 800 ma to an end-of-discharge voltage of 0.6 volt. This was the same end-of-discharge as used in the Phase I testing. It was realized that this end-of-discharge voltage for plate testing in the flooded condition with respect to electrolyte might not represent precisely the same state of discharge as the Phase I testing with the cells in the starved condition with respect to electrolyte. However, it was assumed that any difference resulting from the use of the same end-of-discharge voltage for plate testing in the flooded condition vs. the cell testing in the starved condition would be within experimental error. As can be seen from the capacity data of Table 1, all cells showed capacities comparable to those prior to sterilization (cycle testing prior to Phase I sterilization) and considerably higher than those at the 300th cycle of Phase I. There is no noticeable effect of open circuit or float charge stand time on plate capacity as determined by the test (flooded condition). Neglecting cell S/N 3022 which developed a short (this cell to be discussed in a later section) the sterilized cells showed a 14% reduction in plate capacity when compared with the non-sterilized cells.

3.5 Continued

The effect of state of charge at the time of sterilization on the flooded plate capacity was not clear cut. Plate capacities of 4.29, 4.60, 4.43 and 3.99 ampere hours were realized at 0, 30, 70 and 100% state of charge respectively. Thus there appears to be an increase in plate capacity for 0 to 30% state of charge, then a decrease from 30 to 100%. However, the low capacity observed (4.29 ampere hours) for the 0% state of charge cell might have resulted from the 300 cycles this cell experienced as compared to 1 cycle experienced by the 30, 70, and 100% state of charge cells. Thus if one assumes the capacity degradation of the 0% state of charge cell resulted from cycling, then data shows a definite degradation of capacity as the state of charge increases at time of sterilization. It is interesting to note that the average output capacity of the heat sterilized cells was approximately equal to that of the control cells.

Figures 13 through 26 present typical half cycle charge and discharge voltage curves, of selected cells, obtained during the plate testing. These curves are typical of the curves obtained for all cells tested. As can be seen from the data, the nickel electrode is limiting on discharge. This limiting effect of the nickel electrode was observed on all cells tested. There was little difference observed between cells which had been sterilized and those which had not, except the capacities of cells which had been sterilized were approximately 14% lower than that of those which had not. The data shows that in all cells tested, the major limiting electrode on charge was nickel. It was also noted that in some cells, the cadmium contributed slightly to the limit on charge. This effect was a general observation for all cells tested. Since the nickel electrode contributed to the limit on charbe and was the primary limiting electrode on discharge, and furthermore, the sterilized cells showed plate capacities 14% lower than non-sterilized cells; it appears that sterilization resulted in some degradation of the nickel electrode.

Figures 21 and 22 present the charge and discharge half cycle respectively for cell S/N 3008 which had been charged to the point of gassing on the cadmium electrode. For comparative purposes, Figures 19 and 20 present the normal charge and discharge half cycle for the same cell. A comparison of these two sets of curves shows little difference in measured capacity or limiting effect of electrodes. The only observed difference is the end of charge voltage which was approximately 1.66 for the half cycle charge which was taken to the point of gassing on the cadmium electrode and 1.49 volts for the normal charge cycle. Figures 23 through 26 present similar test data for cell S/N 3012. This cell had experienced the same set of test conditions as cell S/N 3008 during Phase I testing except it had been subjected to sterilization and cell S/N 3008 had not. The same general observation concerning capacity, limiting effect of electrodes and end-of-charge voltage apply to data for cell S/N 3012 as applied to cell S/N 3008.

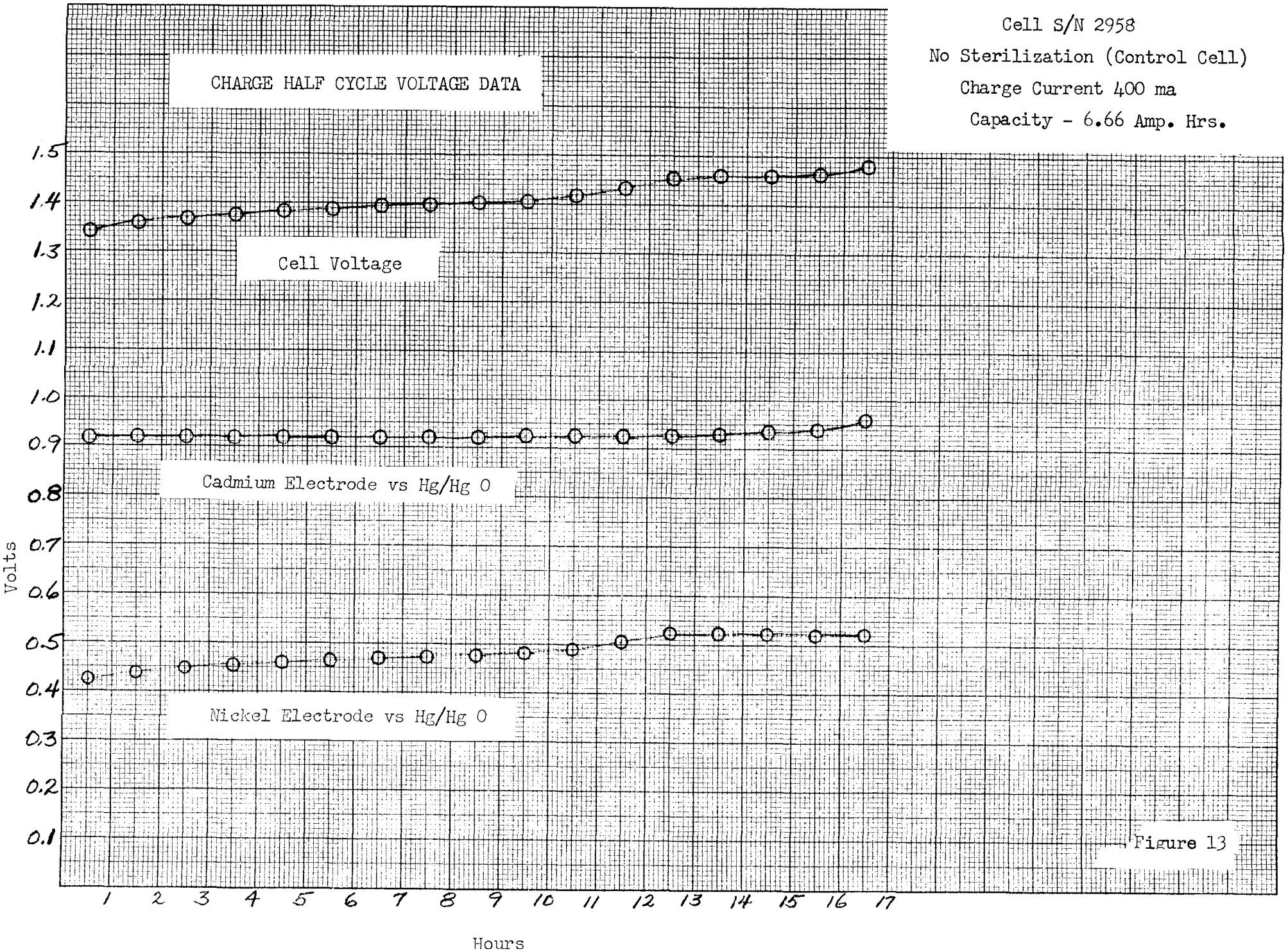

CHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 2958
No Sterilization (Control Cell)
Charge Current 400 ma
Capacity - 6.66 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Hours

Figure 13

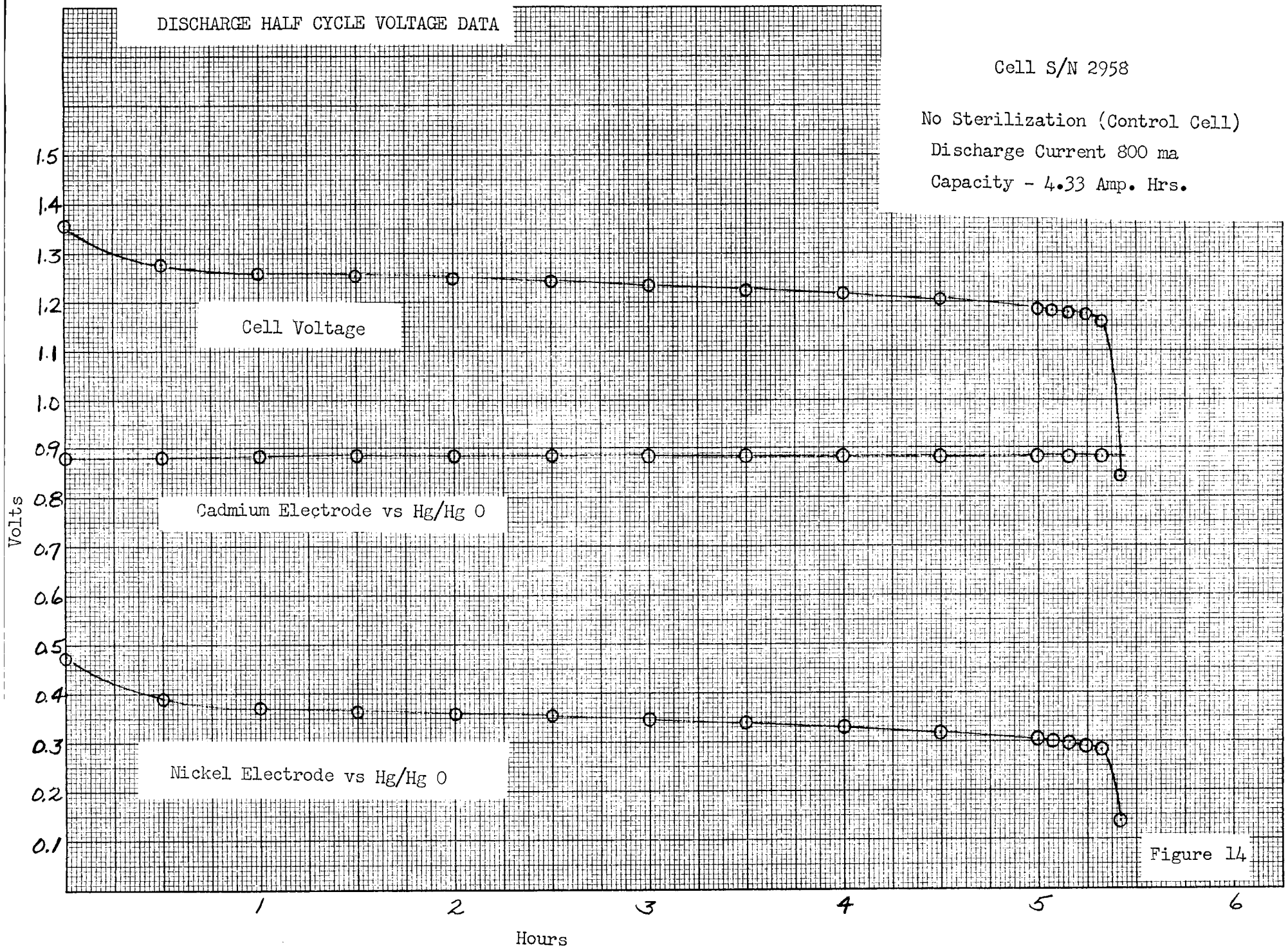

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 2958
No Sterilization (Control Cell)
Discharge Current 800 ma
Capacity - 4.33 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
Hours

Figure 14

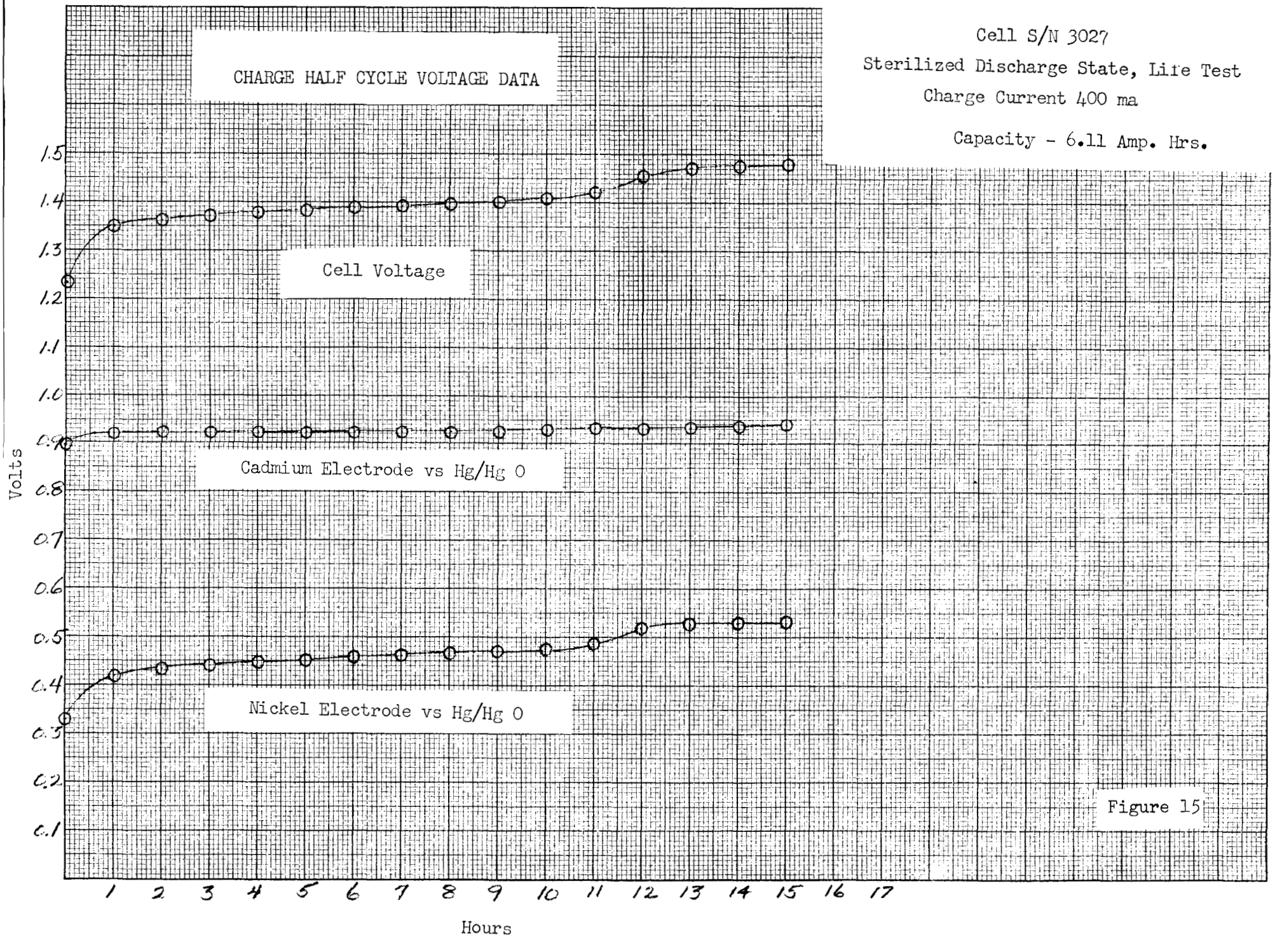

CHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3027
Sterilized Discharge State, Life Test
Charge Current 400 ma
Capacity - 6.11 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
Hours
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Figure 15

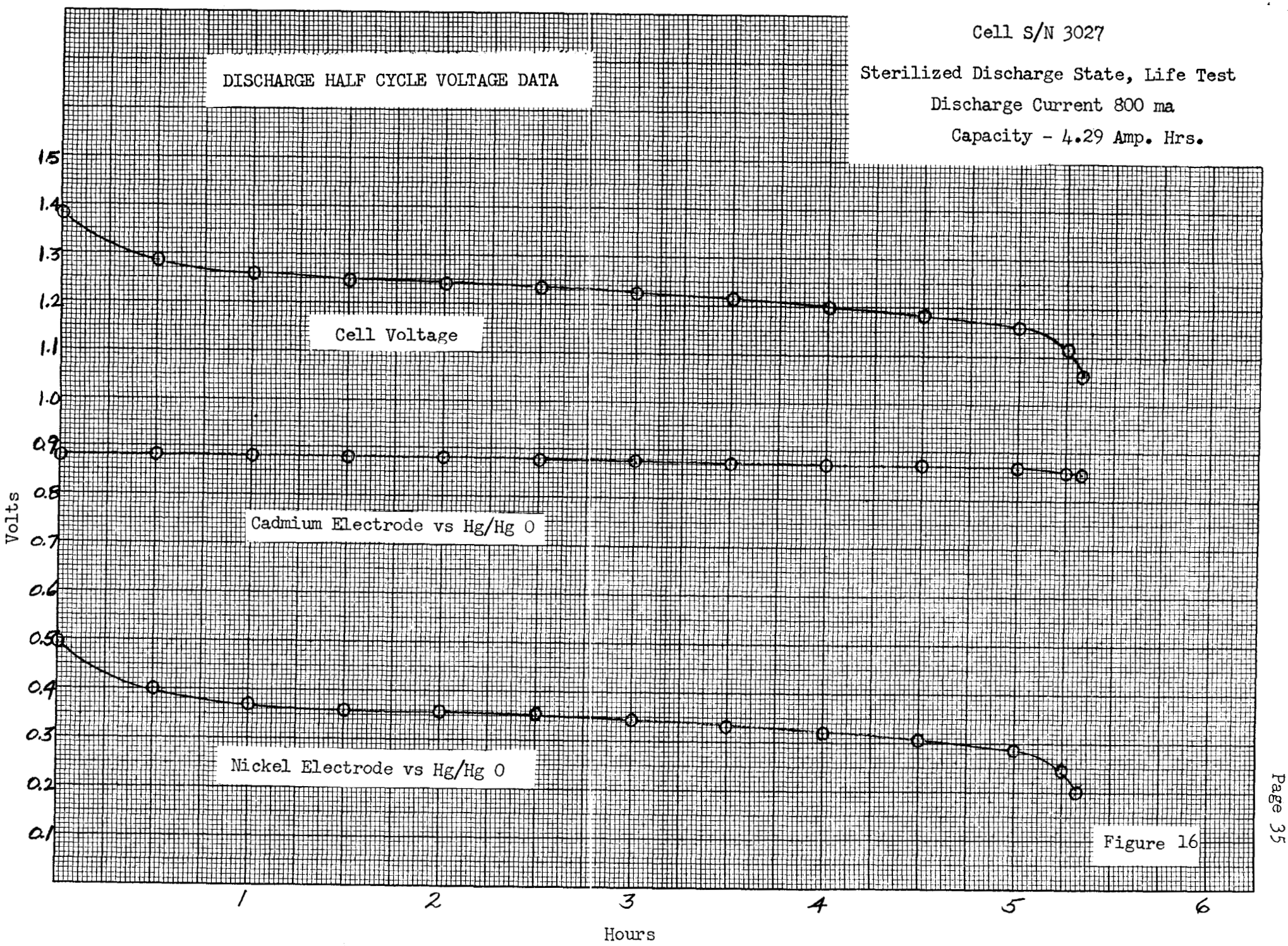

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3027
Sterilized Discharge State, Life Test
Discharge Current 800 ma
Capacity - 4.29 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
Hours

Figure 16

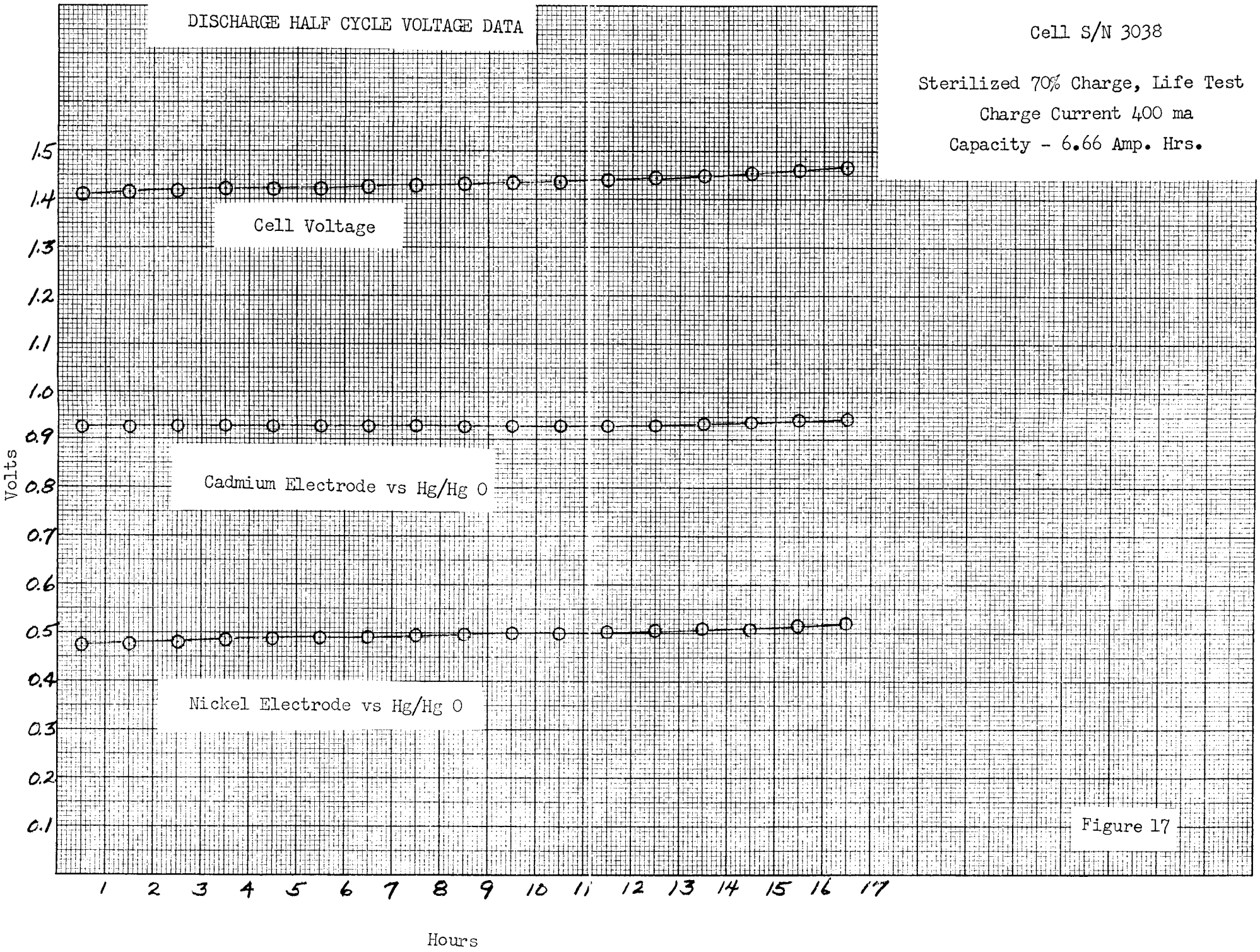

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3038
Sterilized 70% Charge, Life Test
Charge Current 400 ma
Capacity - 6.66 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Hours

Figure 17

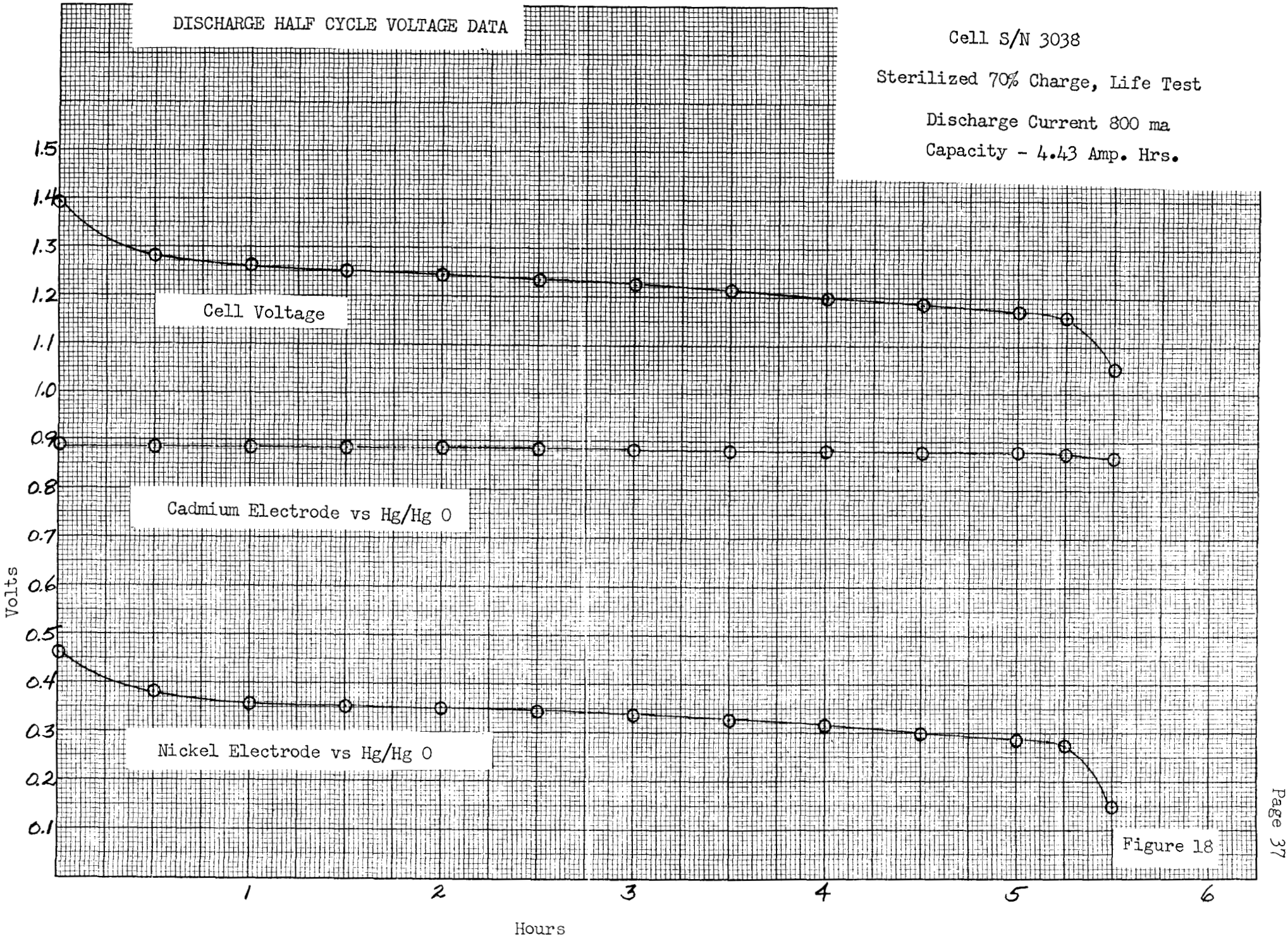

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3038
Sterilized 70% Charge, Life Test
Discharge Current 800 ma
Capacity - 4.43 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
Hours

Figure 18

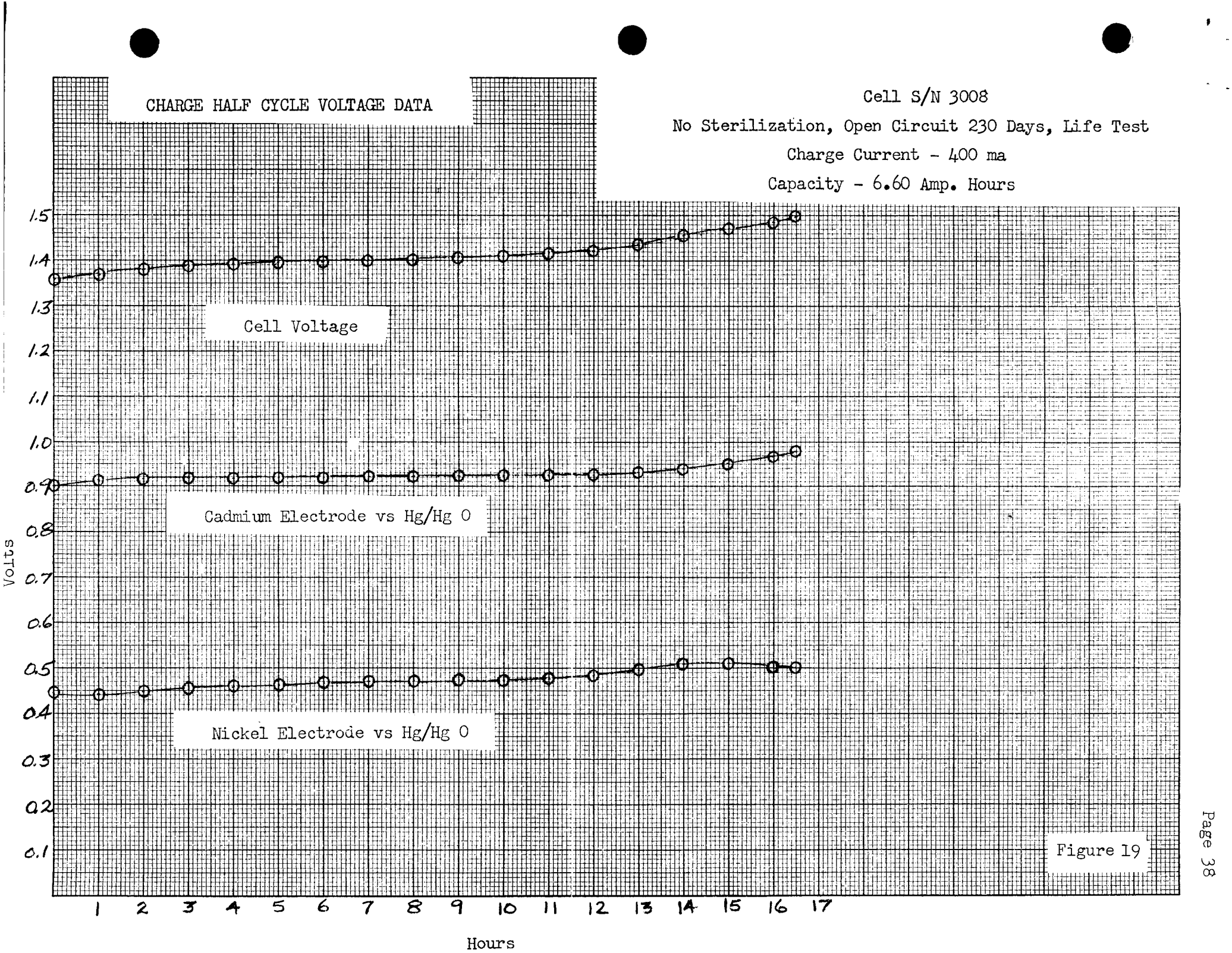

CHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3008
No Sterilization, Open Circuit 230 Days, Life Test
Charge Current - 400 ma
Capacity - 6.60 Amp. Hours
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Hours

Figure 19

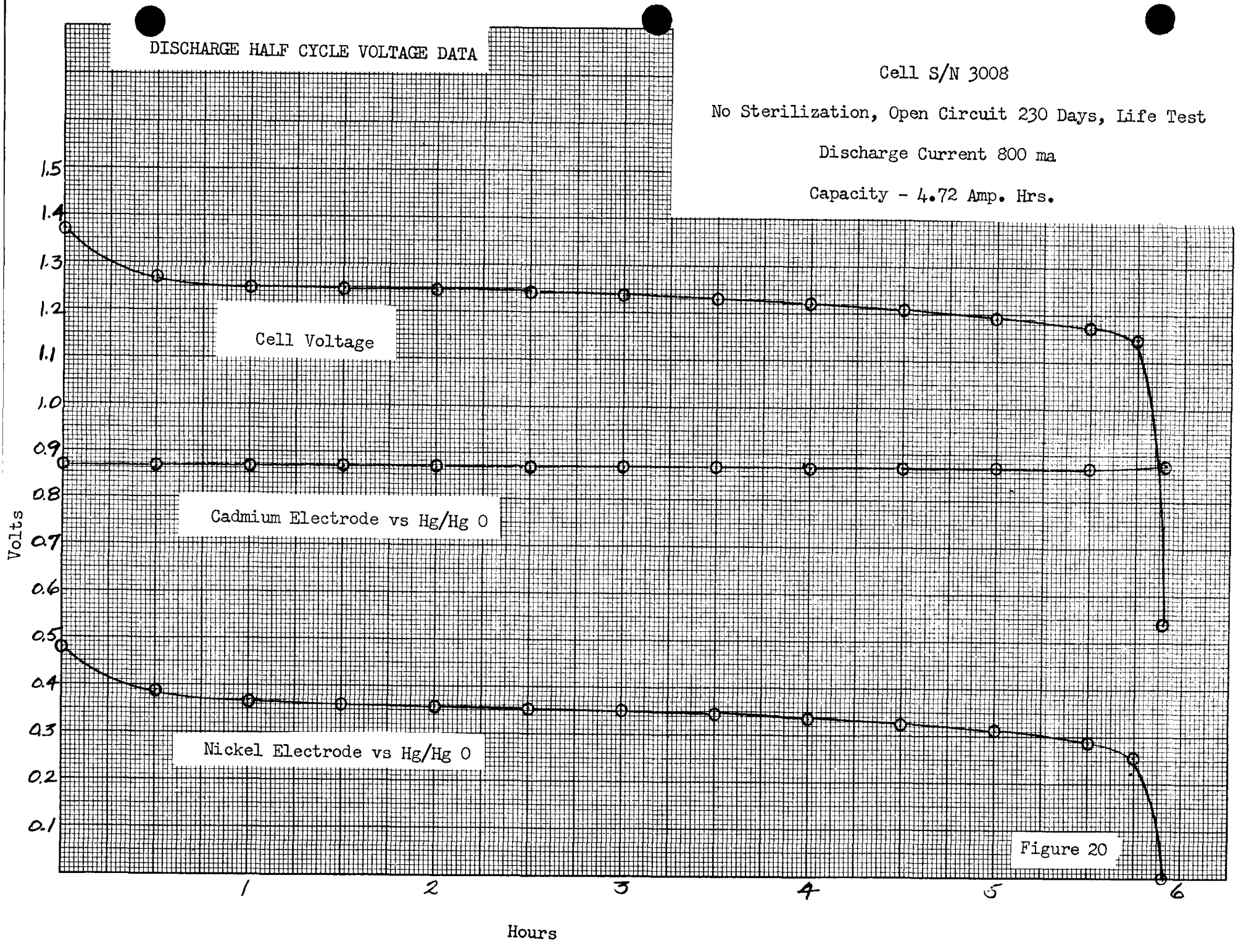

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3008
No Sterilization, Open Circuit 230 Days, Life Test
Discharge Current 800 ma
Capacity - 4.72 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
Hours

Figure 20

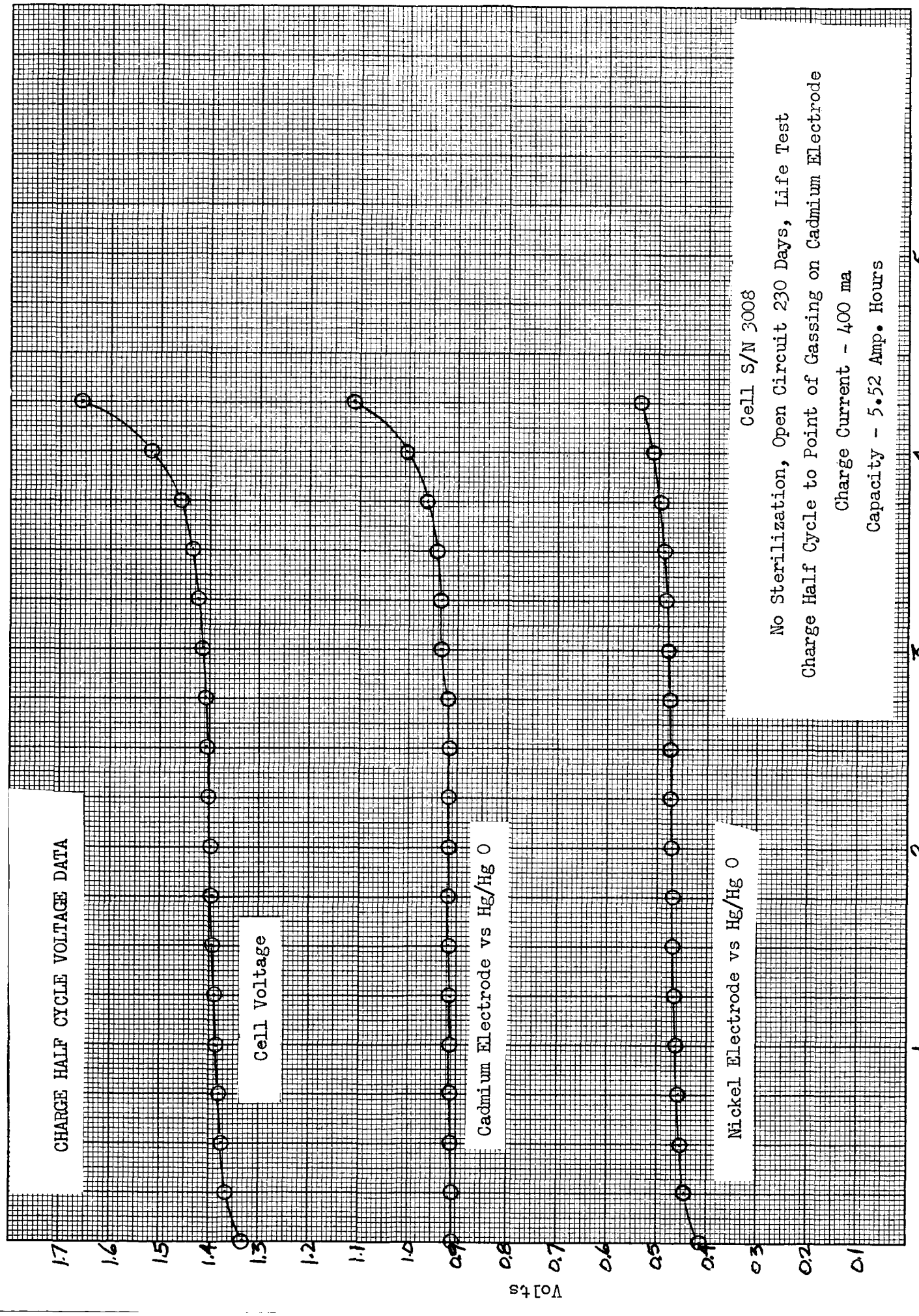

CHARGE HALF CYCLE VOLTAGE DATA
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Cell S/N 3008
No Sterilization, Open Circuit 230 Days, Life Test
Charge Half Cycle to Point of Gassing on Cadmium Electrode
Charge Current - 400 ma
Capacity - 5.52 Amp. Hours
Volts
Hours
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5

Figure 21

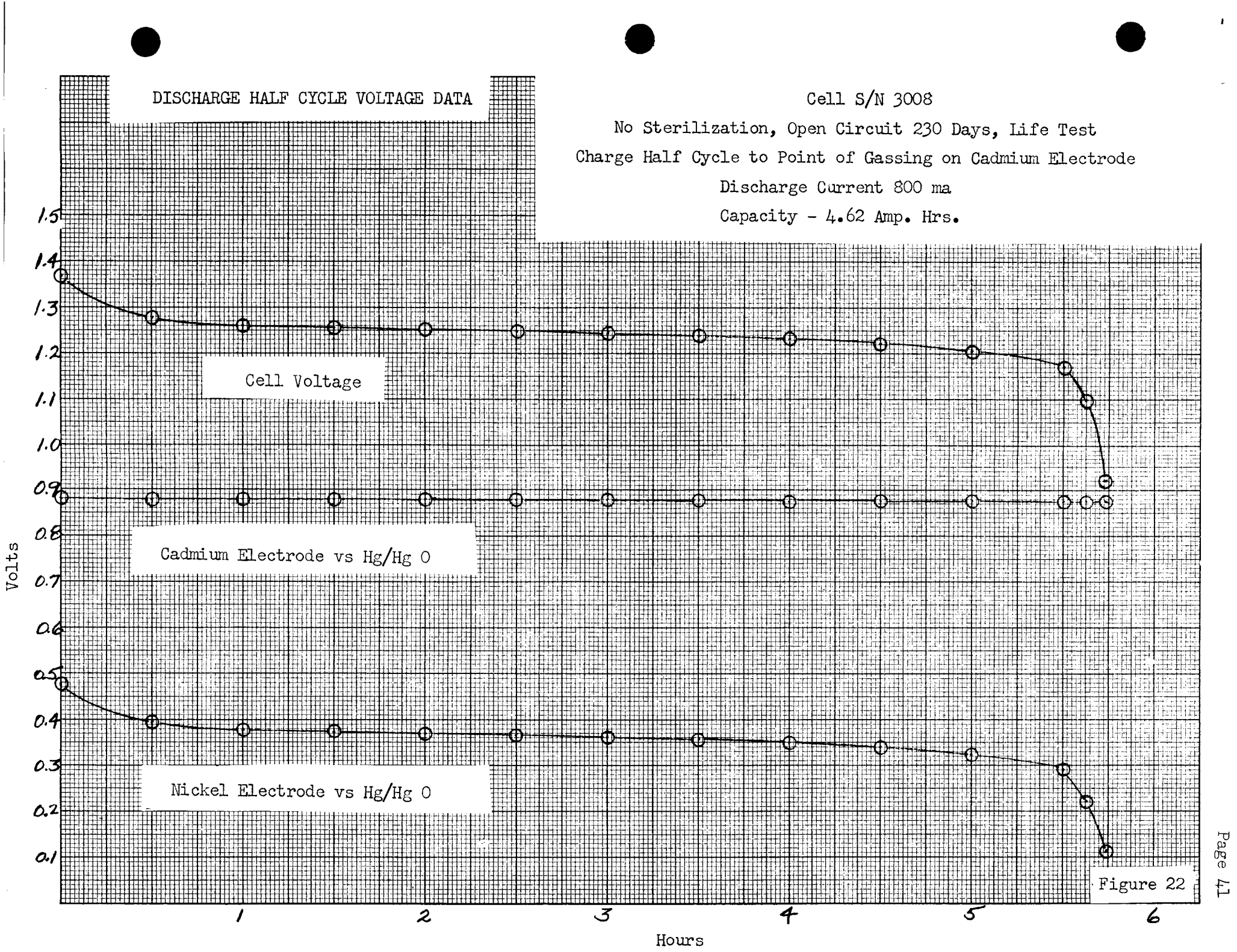

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3008
No Sterilization, Open Circuit 230 Days, Life Test
Charge Half Cycle to Point of Gassing on Cadmium Electrode
Discharge Current 800 ma
Capacity - 4.62 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
Hours

Figure 22

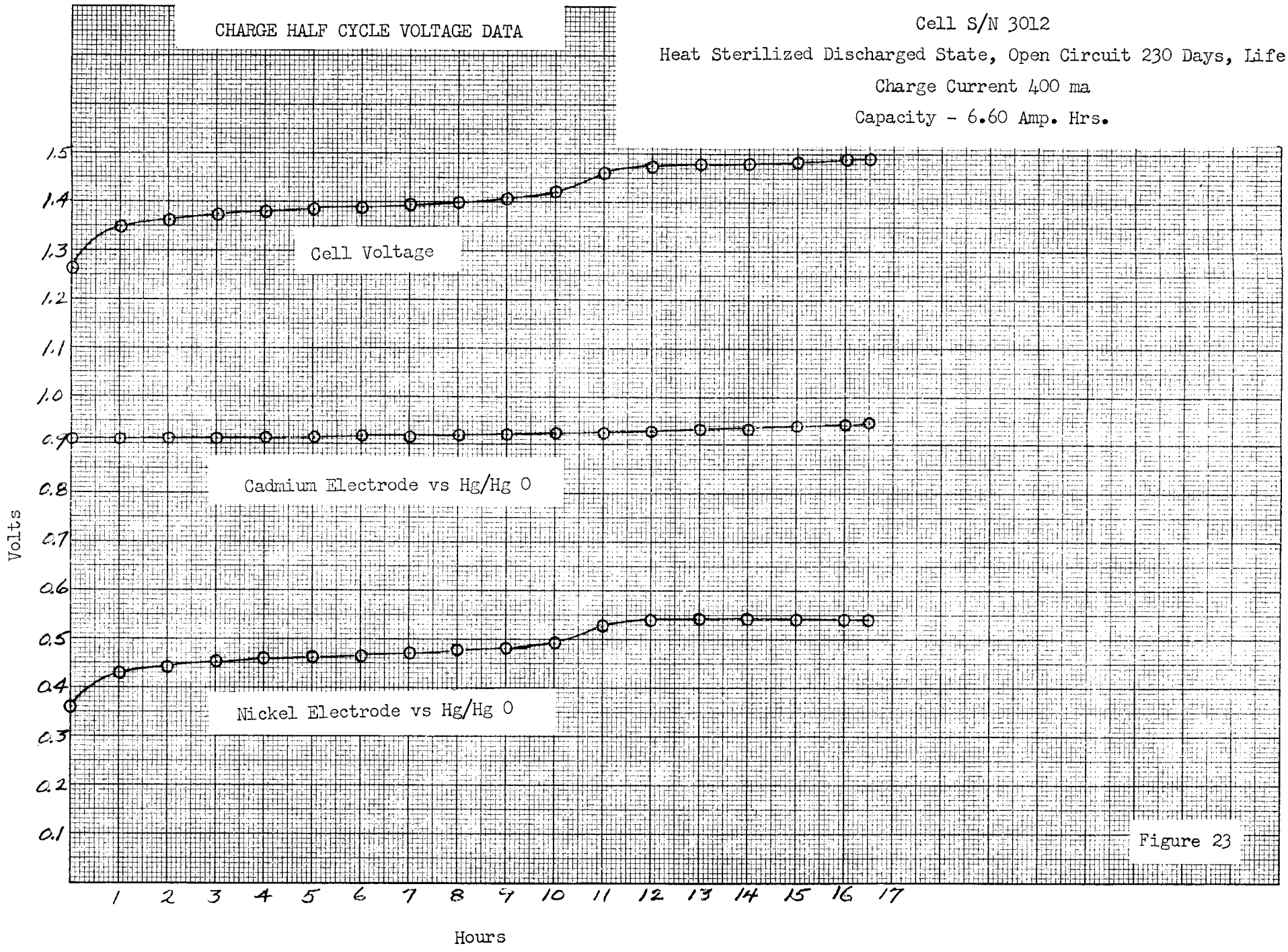

CHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3012
Heat Sterilized Discharged State, Open Circuit 230 Days, Life Test
Charge Current 400 ma
Capacity - 6.60 Amp. Hrs.
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Hours

Figure 23

DISCHARGE HALF CYCLE VOLTAGE DATA

Cell S/N 3012

Heat Sterilized Discharged State, Open Circuit 230 Days, Life Test

Discharge Current 800 ma

Capacity - 4.40 Amp. Hrs.

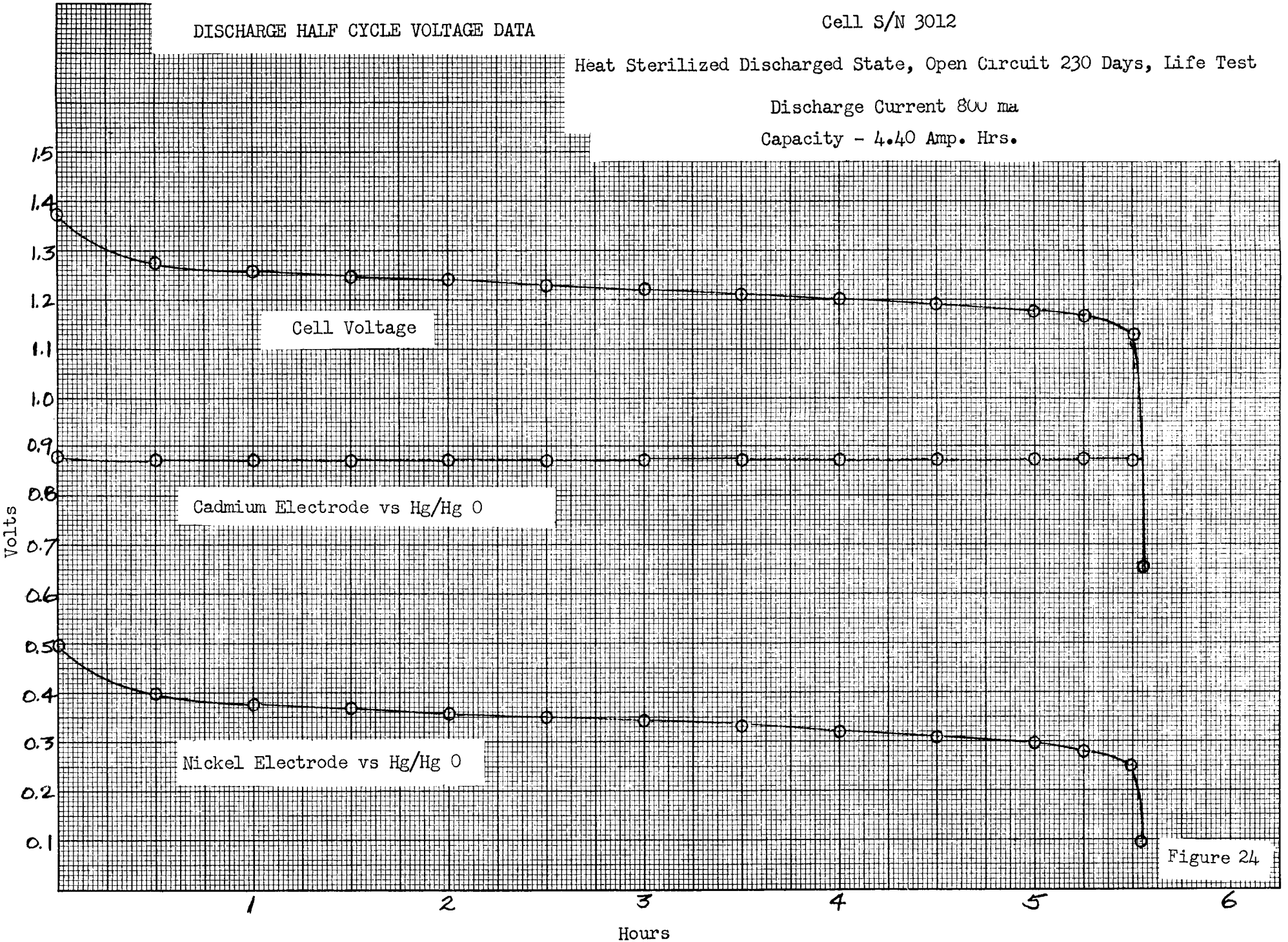


Figure 24

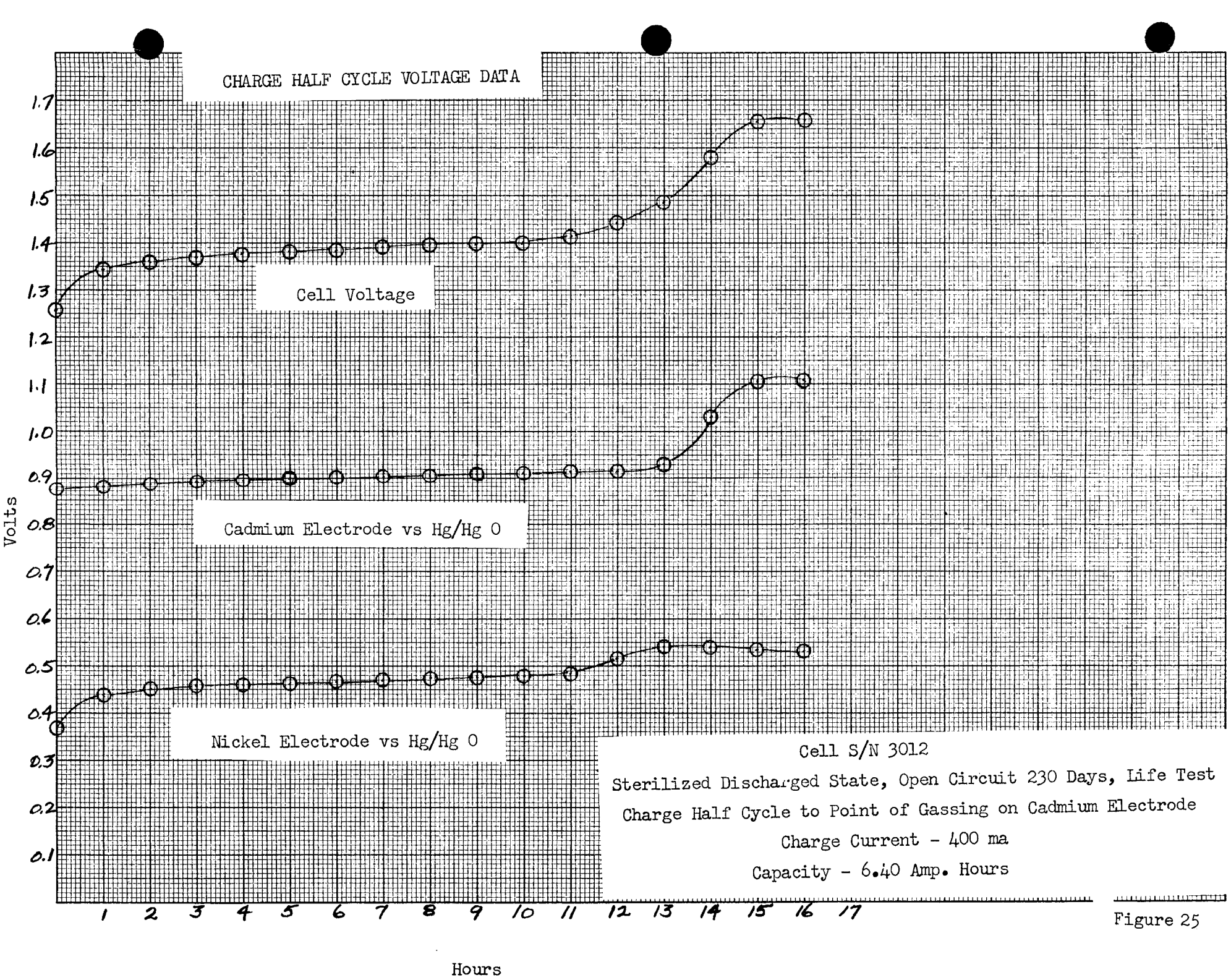

CHARGE HALF CYCLE VOLTAGE DATA
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
Hours
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
Cell S/N 3012
Sterilized Discharged State, Open Circuit 230 Days, Life Test
Charge Half Cycle to Point of Gassing on Cadmium Electrode
Charge Current - 400 ma
Capacity - 6.40 Amp. Hours

Figure 25

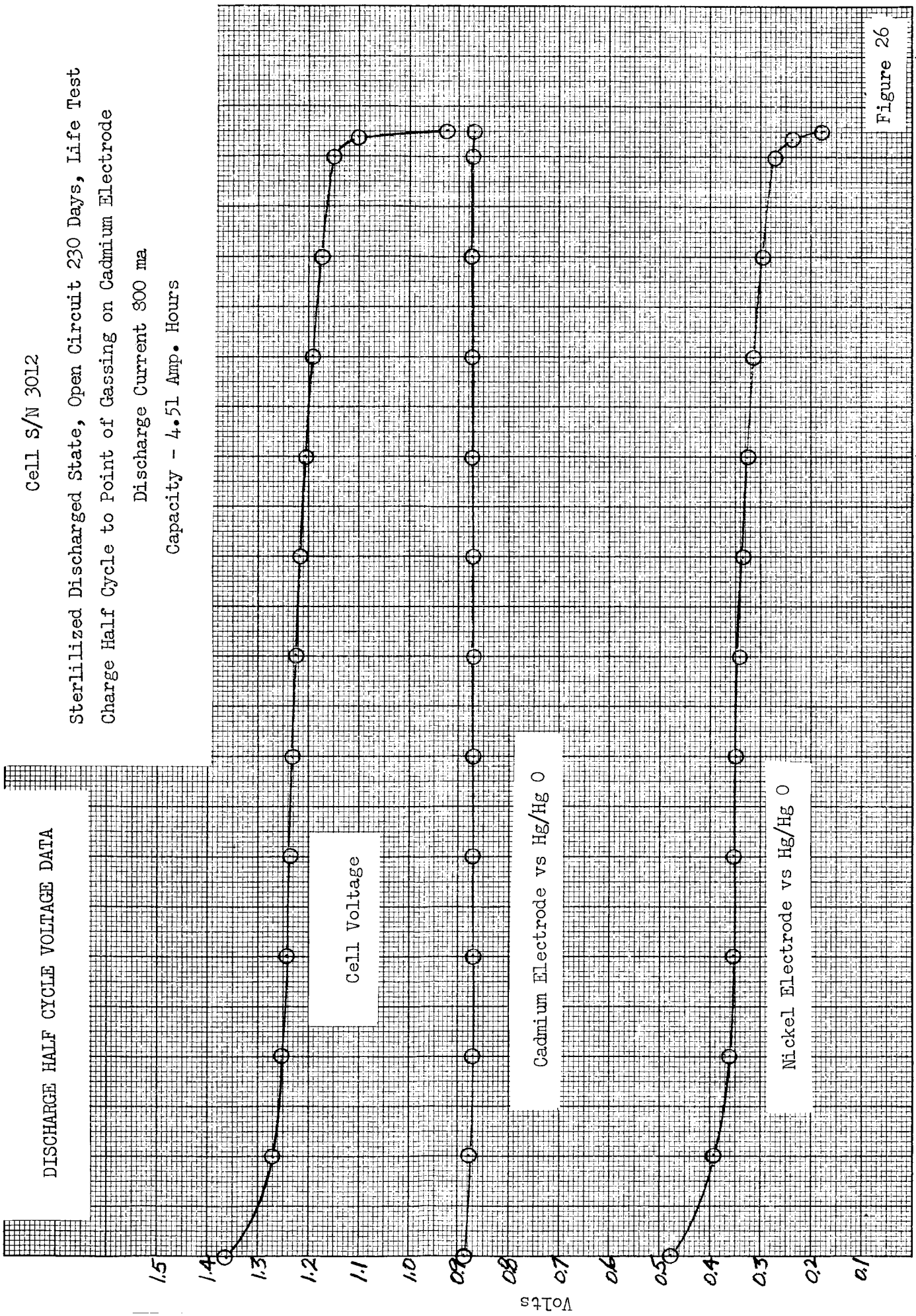

DISCHARGE HALF CYCLE VOLTAGE DATA
Cell S/N 3012
Sterlilized Discharged State, Open Circuit 230 Days, Life Test
Charge Half Cycle to Point of Gassing on Cadmium Electrode
Discharge Current 300 ma
Capacity - 4.51 Amp. Hours
Cell Voltage
Cadmium Electrode vs Hg/Hg O
Nickel Electrode vs Hg/Hg O
Volts
Hours
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6

Figure 26

4.0 CELL S/N 3022 FAILURE ANALYSIS TESTING

This cell had been subjected to the heat sterilization cycles of Phase I and was life cycled only during this phase. In addition, the cell was subjected to electrical performance investigation of Phase III testing. This cell did not show any large deviation from the average output capacity of comparable cells during the Phase I and III testing. The cell did show about 20% less capacity than comparable cells just prior to initiation of failure analysis testing. During the plate capacity testing the cell would not accept a charge. The following sections present the test results of the failure analysis on cell S/N 3022.

4.1 Impedance

The impedance of this sterilized cell was rather high (200 milliohms), but in contrast to the other cells tested that showed a 200^{+} milliohm impedance and zero capacity just prior to failure analysis, this cell exhibited a 2.24 ampere hour capacity. Cell S/N 3017 which was not sterilized but comparable in regard to test history also exhibited a high impedance (250 milliohms) but zero capacity just prior to failure analysis. This is contrary to the generalization made earlier.

4.2 Visual Observations

4.2.1 Case, Leads, Insulator. Upon removal of the electrode-separator assembly from the cell case it was noted that the positive (nickel) lead was very loosely attached to the plate and was partially destroyed. It appeared that the lead at the junction with the plate had been damaged by heat possibly generated by a short. (Figure 27 is a picture of the electrode-separator assembly as removed from the cell.) Further evidence that a large amount of heat was generated in the vicinity of the lead and nickel plate junction was shown by the condition of the three Teflon insulators on top of the cell. The bottom insulator, (Insulator 1 Figure 28) of the top 3, which was in contact with the top of the electrode-separator assembly, was charred and part of it had been destroyed or had melted. The softening or flow temperature of FEP Teflon is between 500° and 550°F. The other two insulators on top of the electrode-separator assembly but further removed from it were also charred and paritally destroyed but to a lesser degree (Insulators 2 and 3 Figure 28). For comparative purposed, insulator 4 of Figure 28 is the insulator which was between the electrode-separator assembly and the cell bottom. Also, the separator in this cell was below the top edge of the plates (See Figure 27) while the separator in all other cells tested extended above the top edge of the plates (See Figure 2). Whether the separator shrank from heat or whether the separator electrode assembly was fabricated this way is not known. Regardless of how the plates became extended above the separator, it could have allowed shorting between plates.

4.2.1 Continued

The case of this cell also showed the black corrosion product on the inside of both the cell top and bottom that had been observed in all the cells tested. However, the deposit, by visual inspection, in this cell was more noticeable and extended about halfway down the side of the case.

4.2.2 Separator. The separator from this cell is shown in Figure 29. The top 1/4 inch of the separator in this cell along its entire length was brittle and hard and was adhering to the cadmium plate in several spots with such force that it prevented its removal in one piece, as shown in Figure 29. It is possible that the insulators of this cell, mentioned in section 4.1.1, actually melted and flowed into the top of the separator and solidified, resulting in the observed adherence of separator to the cadmium plate and its hardness.

4.3 Separator Testing

4.3.1 Tensile Strength, Resistivity and Dimensional Tests. The tensile strength for the 1" x 3" test sample was about 3 Kg. higher than the average of the other sterilized cells. The higher value for this cell probably resulted from the insulator melting and flowing into the separator. The average measured resistivity of this cell was 187 ohm-cm^2 as compared to 208 ohm-cm^2 for non-sterilized and 277 ohm-cm^2 for sterilized cells.

4.4 Electrolyte Chemical Analysis

The carbonate content of the electrolyte for this cell was 3.21 g. as compared to 3.15 g. for the comparable, non-sterilized cell S/N 3017. Both the resistivity of the separator and carbonate content of the electrolyte were slightly higher than the average for the other sterilized cells.

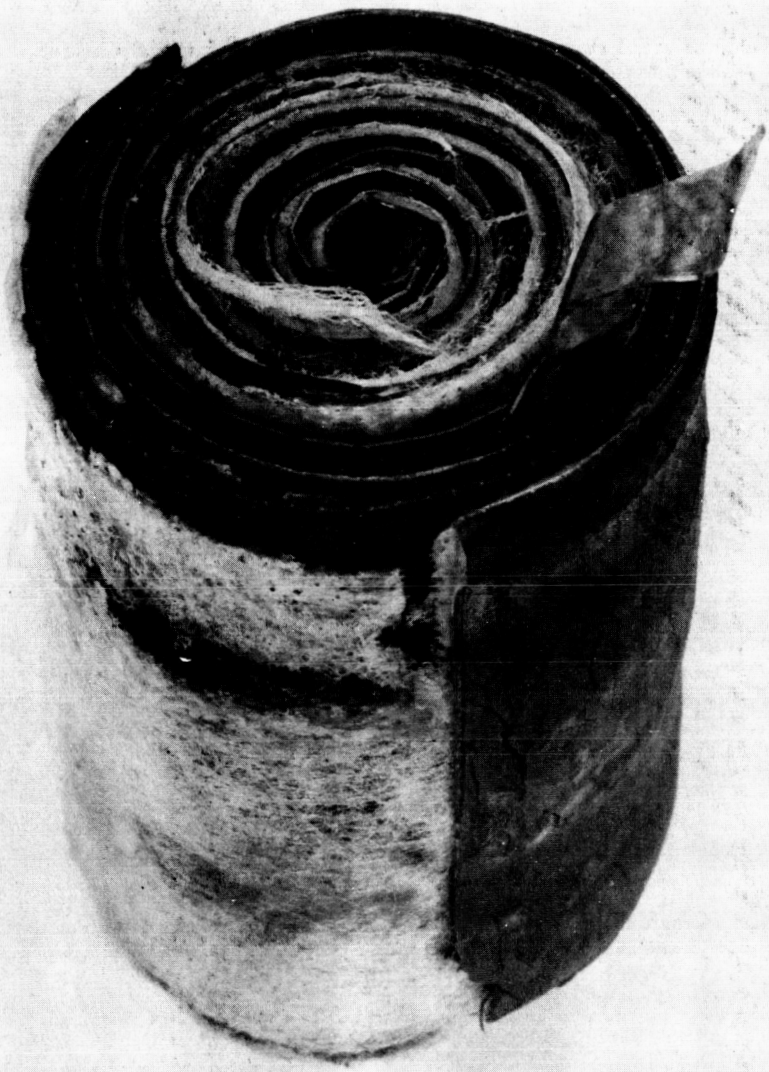
4.5 Electrodes - Plate Testing

Cell S/N 3022 which showed evidence of degradation of the nickel plate electrical lead, insulator, and separator as noted in Sections 4.2.1 and 4.2.2, did not accept a charge when the plates were tested in the flooded condition. However, this cell had accepted a charge just prior to initiating the Failure Analysis test sequence as noted in Table 1. Prior to starting the plate testing the electrical lead had to be resoldered to the nickel plate. Several attempts were made to charge the plates. In the first attempt, the charge half cycle started in a normal manner. That is, the nickel plate showed a voltage of about +0.4 volt with respect to the reference electrode (Hg/HgO), and the cadmium plate had a voltage of about -0.9 with respect to the same reference. After about 2 hours of charge at 400 ma, the voltage of the nickel plate, with respect to the reference, started to move in the negative direction and eventually approached the value of the

4.5 Continued

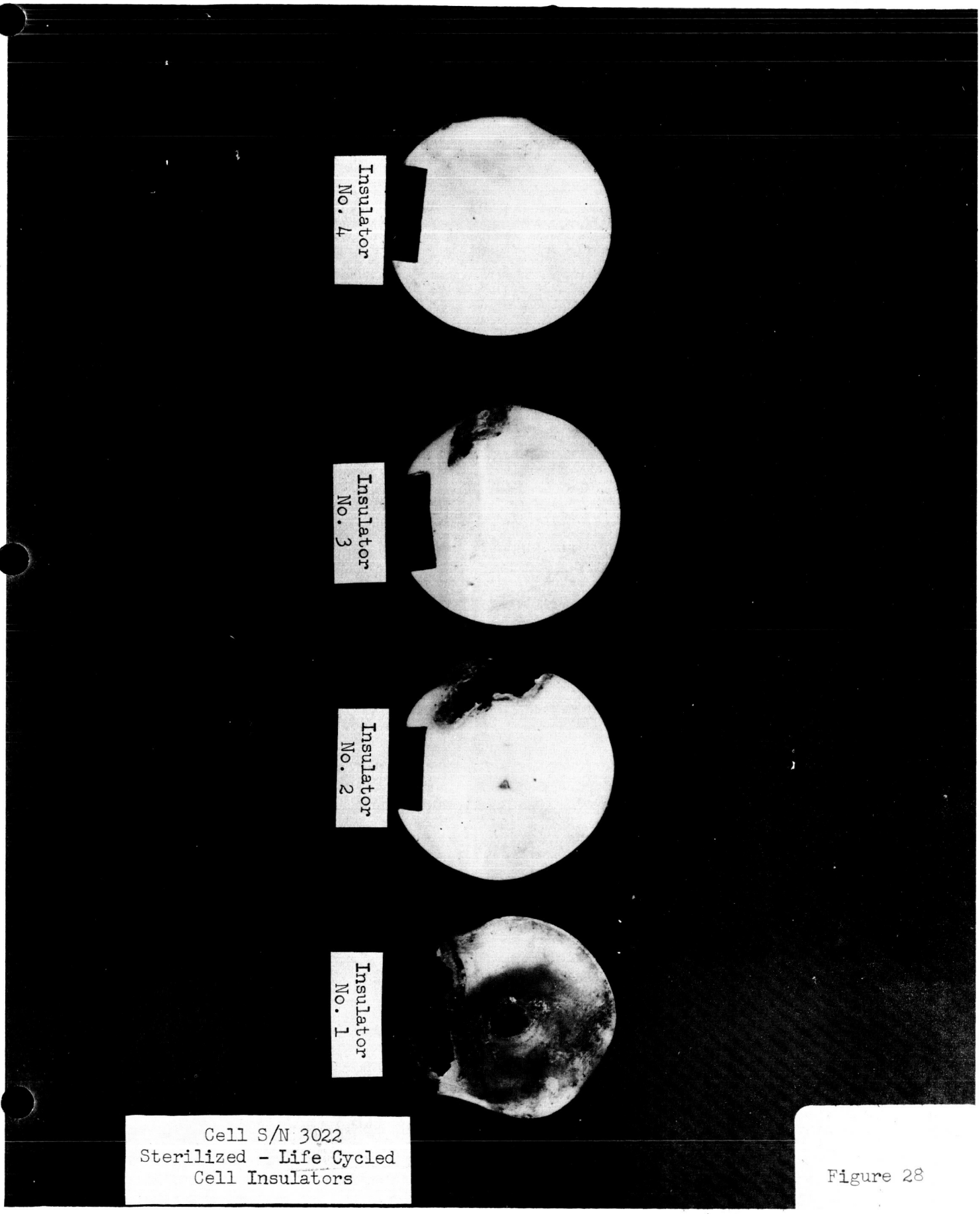
cadmium plate. That is, it approached a value of approximately -0.9 volt with respect to the reference. The voltage behavior of the nickel plate was confirmed by the cell voltage which started at about 1.3 volts and approached 0.0 volts as the nickel plate approached the voltage of the cadmium plate. Open circuit voltage after the first charge was approximately -0.9 volt, with respect to the reference, for both the nickel and cadmium plates and 0.0 volt for cell voltage. Subsequent attempts to both charge and discharge the plates of this cell did not alter the voltages of the first attempt of charging. The plate potentials remained at -0.9 volt with respect to the reference and the cell voltage remained at 0.0 volt. The system was investigated for possible shorts, and a new separator was used for each charge-discharge attempt.

An unusual amount of black residue was noted on the separators and in the electrolyte solution used in plate testing. Also, a large amount of the same material was observed in the solution obtained from the electrolyte leaching process. The black residues were filtered from the electrolyte leach and plate testing solutions and analyzed by emission spectrographic and x-ray diffraction techniques in an attempt to determine the cause for the plates not accepting a charge. The results of the emission spectrographic analysis are presented in Table IV. The emission spectrographic analysis was performed by Pacific Spectrochemical Laboratory, Inc., Los Angeles, California. The data shows the major metallic components to be nickel and cadmium which is what would be expected for a normal cell. X-ray diffraction analysis of the combined residues remaining after the spectrographic analysis by Sloan Research Industries, Inc., of Santa Barbara showed the major component was cadmium hydroxide. Also found to be present in intermediate concentrations were cadmium carbonate and nickel metal. The results of the x-ray analysis are presented in Table V. The formation of cadmium carbonate in cells and its effect on cell performance are not clearly understood. Therefore, the results of the spectrographic and x-ray analysis did not produce any conclusive evidence as to the cause of cell failure. The data obtained indicates that even if an inferior solder joint resulted when the nickel lead wire was resoldered to the electrode, this joint could not have been responsible for the failure. It is possible that the cadmium carbonate found by x-ray diffraction contributed to the failure of the cell to accept a charge.



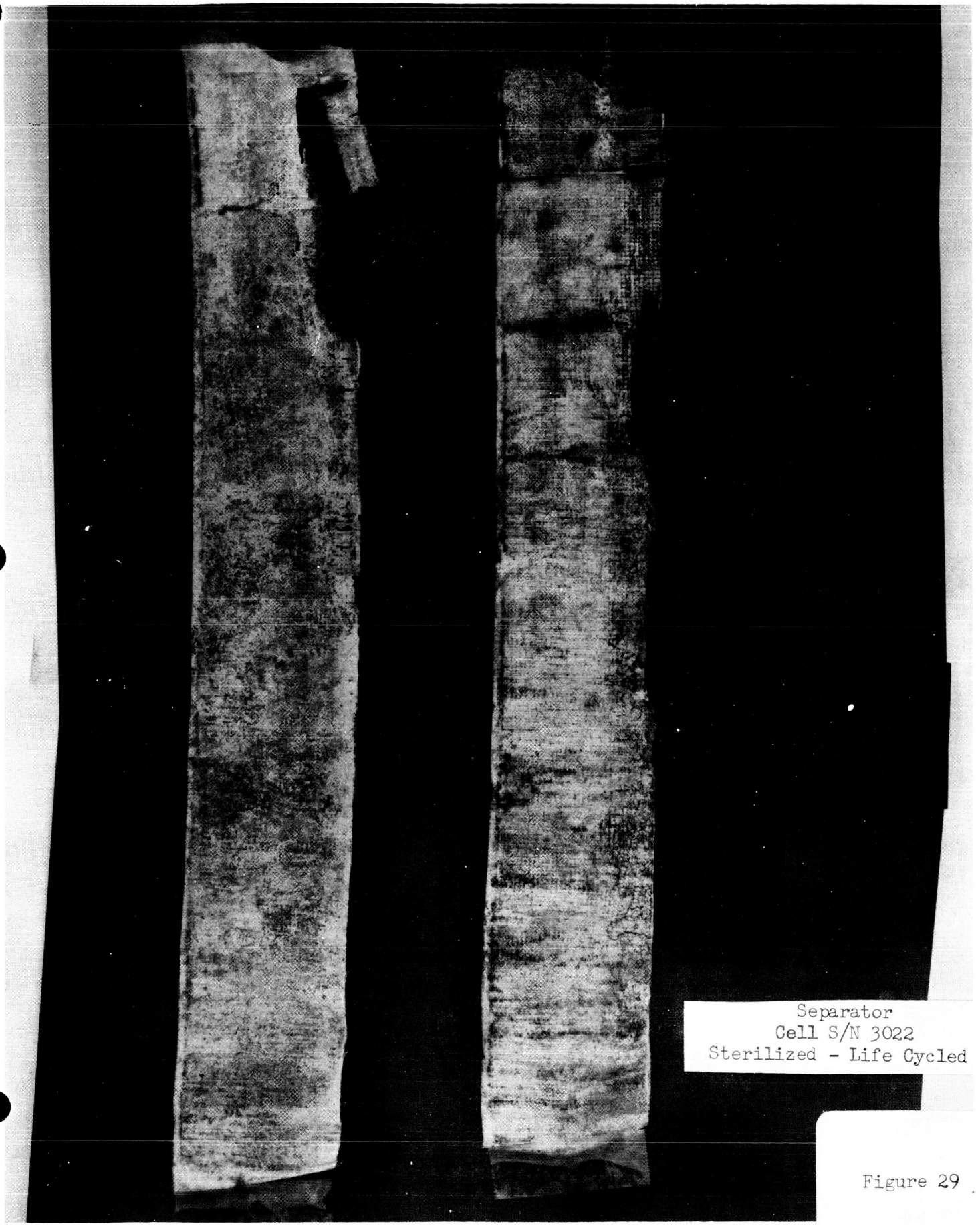
Separator-Electrode Assembly
Cell S/N 3022
Sterilized - Life Cycled

Figure 27



Cell S/N 3022
Sterilized - Life Cycled
Cell Insulators

Figure 28



Separator
Cell S/N 3022
Sterilized - Life Cycled

Figure 29

TABLE IV

Semiquantitative Spectrographic Analysis of Residues from Cell S/N 3022

Metallic Element	RESIDUES First Leach (%)	Second Leach (%)	Plate Test (%)
Nickel	8.0	46.0	21.0
Cadmium	17.0	20.0	12.0
Iron	1.3	2.2	0.95
Cobalt	0.52	3.4	1.8
Magnesium	0.54	1.6	0.46
Calcium	0.16	0.16	0.35
Chromium	0.017	0.37	0.21
Silicon	0.60	3.7	0.98
Boron	0.072	0.50	0.14
Manganese	0.024	0.10	0.040
Lead	0.092	0.090	0.28
Aluminum	0.17	0.55	0.50
Tin	nil	nil	nil
Copper	0.030	0.17	0.034
Silver	0.022	0.055	0.030
Zinc	0.12	0.21	nil
Titanium	trace	trace	0.035
Other elements	nil	nil	nil

TABLE V

X-Ray Diffraction Analysis of Residues* From Cell S/N 3022

d-Spacing A	Intensity	$Cd(OH)_2$	Ni	$CdCO_3$
4.63	100	X		
3.78	20			X
3.02	40	X		
2.93	40			X
2.71	10			X
2.53	80	X		
2.34	40	X		
2.07	10			X
2.03	30		X	
1.86	50	X		X
1.82	20			X
1.74	20	X	X	
1.51	10	X		
1.44	10	X		
1.39	10	X		

*Because the results of the emission spectrographic (Table 4) analysis showed the three samples contained the same metallic components, the portions of the samples remaining after the spectrographic analysis were combined for the X-ray diffraction analysis.

5.0 DISCUSSION

The plate testing results coupled with the impedance test indicate that either the separator or a passivating coating on the plate surfaces, which was removed when flooded with electrolyte, was partially responsible for noted cell failures and lowered capacities. Also, the plate capacity test when considered alone showed lower capacities for sterilized cells, and that the nickel electrode contributes to the limit on charge and is the major limiting factor on discharge indicating some degradation of the nickel electrode results from the sterilization process. The separator's contribution to cell failures and observed lower capacities is difficult to interpret. Those cells showing a high impedance (200 milliohms or better) do not show a corresponding high separator resistivity, and some cells exhibiting low impedance (12 to 100 milliohms) show high (500^+ ohm-cm^2) resistivities. The separator resistivities were measured in the flooded condition with respect to electrolyte as compared to the starved condition for the cell impedance measurements, and the separators were not under compression for the resistivity test whereas they were for the impedance measurements, which could possibly account for some of the observed differences. Another possible explanation of the lack of correlation between measured impedance and resistivity, if indeed the measured impedance was a direct result of separator resistivity, is the fact that the impedance, in portion, is a measure of the average impedance of the entire separator whereas the resistivities were measured on samples taken from selected positions of the separator; and it is possible the resistivity samples were not representative. Non-representative resistivity samples could also account for the resistivity variations noted both within and between separators. It is also possible that the high (200^+ milliohm) observed impedances could have resulted from a distribution of the electrolyte within the cell assembly such that the separator was in a more starved conditinn than normal. The distribution of the electrolyte in cells showing high impedance values could have been such that it was predominantly in the pores of the plates. There was no correlation between sterilization and cell impedance and separator resistivity. It is possible that correlation was obscured by the effects of non-uniform distribution of electrolyte in separator, non-representative separator resistivity samples, etc.

Chemical analysis of the electrolyte showed essentially the same amount of carbonate and hydroxide for both sterilized and non-sterilized cells. Although carbonate could possibly have contributed to the observed cell failures and lowered capacities, no conclusive dependence was established. The separator tensile strength test showed a definite relationship with sterilization. The separators from those cells which had been sterilized showed lower tensile strengths than comparable cells which had not. This lower tensile strength coupled with the observed stiffness of separators from cells which had been sterilized definitely established a separator degradation caused by sterilization. The output capacities measured during the plate capacity testing were lower for sterilized than comparable non-sterilized cells but equal to the control cells. This effect

5.0 Continued

of lowered capacities for sterilized cells is opposite to that noted from cell capacity measurements made just prior to failure analysis testing. This difference in capacity could be explained by the fact that the cell capacity measurements were made with the cell intact (separator starved with electrolyte), whereas the plate capacity measurements were made in the flooded (with respect to electrolyte) condition.

The x-ray analysis and spectrographic analysis did not produce any conclusive information as to the reason cell S/N 3022 would not accept a charge during the plate testing in the flooded condition. The nickel electrode in this cell acted as if it had become coated with cadmium. The potential of the nickel plate became approximately -0.9 volt with respect to the reference electrode (normal +0.4 volts) when placed on charge which is about the same voltage (-0.9 volt) of the cadmium plate. The nickel maintained this voltage on subsequent attempts to charge and discharge the plates. Because the residues were filtered from the leach and plate testing solutions, they were undoubtedly a composite of material that sloughed off of both plates and thus the origin of the species found by x-ray analysis could not be determined.

6.0 CONCLUSION

The results of the failure analysis testing showed some effects of sterilization on the separator, electrolyte and plates which could be related to cell failure or observed variations in capacity. Although some trends were established, no on factor could be established as the major cause of cell failure or observed variations in capacity. The data seems to indicate there are a number of factors which contributed to cell failure.

Separator degradation resulting from sterilization was definitely established. Separators from cells which had been sterilized in the discharged state showed a tensile strength which was approximately 32% lower than cells which had not been sterilized. This value is based on data from the large size (1" x 3") test samples. There was also an observed stiffness of the separator in cells which had been sterilized. Although little data was obtained on separators from cells which had been sterilized in the discharged state, visual inspection of the separators from these cells showed the degree of separator degradation for sterilized cells increased as the state-of-charge increased. The dimensional measurements showed that there was slight shrinkage (1.5%) in the width of the separators which had been sterilized, and they also show a much larger variation in thickness and an average thickness greater than non-sterilized cells.

6.0 Continued

The impedance measurements are lower for the sterilized than for non-sterilized cells if all cells are considered. Comparison of the capacities of the cells measured prior to failure analysis with the corresponding impedance values shows that the low impedance reflects itself in a higher output capacity. If the impedance values are compared to the plate capacity test, the reverse occurs or the low impedance reflects itself as a low output capacity. The impedance measurements were made with the cell intact, and the differences could be explained as variations in separator thickness, distribution of electrolyte in cell, or a passivating layer on one or both electrode surfaces which was removed when electrodes were flooded with electrolyte for plate testing. Also, new separators were used for plate capacity testing.

The chemical analysis of the electrolyte showed that sterilized cells had on the average a 20% higher carbonate content and a corresponding 14% lower capacity on plate testing. However, the control shows a 23% higher carbonate content than the sterilized cells with a corresponding 9% higher capacity than the sterilized cells. Since only one control cell was taken for carbonate comparison, it may not have been representative. If it was, however, carbonate data when compared to the plate capacity data indicates carbonate formation is detrimental to cell performance and to the nickel electrode. However, due to the fact that the leaching process for removal of the electrolyte from the electrode-sepaarator assembly was altered several times to improve the technique, the results, although analytically correct, may be in error due to the alterations made in the electrolyte leaching process. More work is required in order to confirm and establish the role of carbonate content of electrolyte on cell performance, and to determine if the sterilization process does indeed promote the formation of carbonate.

The resistivity measurements show considerable variation within a separator and also between separators. The data obtained does not firmly establish if sterilization has any effect on the resistivity of the separator or if it ultimately reflected itself on cell performance. The variations noted in the resistivity data probably arose from variations in the thickness of the separator and the adherence of active electrode materials to the surface of the separator.

The plate capacity measurements show that the sterilized cells had an average output capacity 14% lower than non-sterilized cells and approximately equal to the capacity of the control cell. This is the reverse of that experienced prior to failure analysis, that is, prior to failure analysis, the sterilized cells showed a slightly higher capacity than non-sterilized cells. This difference can be partly attributed to the fact that plate capacity measurements were made in the flooded condition (with respect to electrolyte) while the capacity measured

6.0 Continued

prior to failure analysis were made with the cell intact and starved with respect to electrolyte. Also, the plate capacities were measured with new separator. Any passivating layer on electrode surfaces which might have been present during cell capacity measurements could possibly have been removed when flooded with electrolyte for plate capacity measurements. All or some of these reasons could have been responsible for the differences in the observed cell and plate capacity measurements. The plate capacity measurements did establish that the sterilized cells showed lower capacities than the non-sterilized cells and that the nickel electrode contributed to the limit on charge and was the major limiting factor on discharge. This suggests that the sterilization process degraded the nickel electrode in some manner.